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K. Gossner

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OVER-TENSION AND INTERFACIAL CHEMISTRY

Dr. Konrad Gossner

OVER-TENSION AND INTERFACIAL CHEMISTRY

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To Professor Georg-Maria Schwab,

to whom I should like to express my gratitude for his kind help and assistance, and for the considerable interest which he always showed regarding my work.

My thanks are also extended to all of my co-workers, who contributed to the success of my study by their assistance in the experiments. Dr. C. Löffler and Messrs. U. Freyer, F. Mansfeld, and C. P. Hodum lent especially valuable aid in the over-tension experiments.

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TABLE OF CONTENTS

INTRODUCTION.....1

CHAPTER I. HETEROGENEOUS PROCESSES.....3

CHAPTER II. CONTACT EFFECT PARAMETERS.....7
1. Geometric Factors.....7
2. Electronic and Chemical Factors.....9
3. Factors of the Real Structure.....12

PART A: THE CONTACT CHEMICAL BASES OF ELECTROLYTIC DISSOCIATION OF HYDROGEN

CHAPTER III. HYDROGEN OVERTENSION.....13
1. The Cathodic Hydrogen Discharge as a Test Reaction.....13
2. Reaction Mechanisms.....16
3. Current-Potential Relationships.....22

CHAPTER IV. ELECTRODE POTENTIALS.....26
1. Circuit Arrangement.....26
2. Measurement Circuit Potentials.....27
3. ζ-Potential. Reaction Kinetics with Regard to Hydrogen-Ion Concentration.....31

CHAPTER V. OVERTENSION AND CONTACT SPECIFICITY.....40
1. Theoretical Exchange Flux Densities.....40
2. Frequency Factors and Activation Energies.....42
3. Temperature-Dependence of Exchange Flux Densities.....44

CHAPTER VI. REPRODUCIBLE OVERTENSION MEASUREMENT.....48
1. Abrasion Method.....49
2. Measured Values in Abrasion Tests.....53
3. Discussion of the Abrasion Method.....57

PART B: HYDROGEN OVERTENSION IN VARIOUS METALS AND ALLOYS

CHAPTER VII. OVERTENSION SYSTEMS.....62

CHAPTER VIII. OVERTENSION FINDINGS.....66
1. Remarks on Experimental Procedure.....66
2. Measurement Data (Current-Potential Curves).....69
3. Kinetic Parameters.....77
4. Discussion.....84
5. Conclusions Regarding the Absolute Potential.....87

CHAPTER IX. CONTACT CHEMICAL EVALUATION.....89
1. Interaction Energy and Electronic Factor.....89
2. Discussion of Frequency Factors.....99

REFERENCES.....102

INTRODUCTION

Among the physical and chemical processes, two groups occupy /1* a special position by virtue of their mechanisms: the heterogeneous catalyses and the electrode processes. In both of them, the important reaction steps take place in the interfacial regions of condensed phases, whose components play a critical, yet only intermediary role in the event. Processes of this type require a specific experimental and theoretical system of problematics. This problematics gives rise to a uniform classification and method of viewing the processes (including the special case of adsorption) as heterogeneous or contact reactions.

In the present paper, an attempt is made to achieve an understanding of heterogeneous reactions from two aspects: first of all, their nature and their problematics are sketched in a form which is as comprehensive as possible, and basic viewpoints for their investigation are given. In this connection, the opportunity arises to lay the groundwork for a theory of the contact effect, the real heart of any theory of the contact process.

The major portion of the work is then devoted to a discussion of electrode reactions as contact-determined processes. This is done using the example of the electrochemical dissociation of hydrogen, which assumes a central position and is also of particular interest from the standpoint of catalyses.

First of all, the theory of hydrogen overtension, i.e., the hydrogen dissociation reaction, is developed in a formulation adequate for its consideration as a contact reaction, which takes into account the actual conditions in the electrode systems and provides valid relationships for comparison studies. A critical survey reveals that previous comparison methods are essentially useless, because they use theoretically inaccurate assumptions, insufficient measurement values, or (for lack of more exact measured values) overly rough averages and simplifications. With regard to these developments, there is a discussion of the potential conditions in electrode systems, including the absolute potentials, in which didactic viewpoints are also expressed.

In this regard, there is a discussion of a method of investi- /2 gation which has made it possible for the first time to obtain a completely reproducible measurement of this electrode reaction and indeed, of a heterogeneous process. It should be noted in

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* Numbers in the margin indicate pagination in the foreign text.

this regard that a principle hindrance to the understanding of contact reactions thus far has been the unavailability of measurement data. The new measurement method is distinguished by its highly simplified and time-saving method of experimentation.

The relationships which are developed are then given concrete application in a discussion of comparison studies of the overtension behavior of metals in the first subgroup and certain alloy series in the latter. The corresponding measurements are partial data from a long-term research program dealing with the systematic study of the contact behavior of metals and alloys. The findings which are presented offer uniform relationships which are applicable primarily to the electron structure of the contacts. On the basis of these data, a new method for estimating the possible extreme values of the absolute potentials is discussed. In addition, initial contributions are made to the previously very little understood behavior of the so-called throughput factor. This value is closely related to the structure of the electrode interface; its detailed study promises to provide important information regarding the latter.

CHAPTER I

HETEROGENEOUS PROCESSES

Every complete contact process consists of several stages: /3
these can be divided into transport processes and interaction processes according to the following system:

Transport Processes		Interaction Processes
1) Application of the Substrate	2) Inward Diffusion of the Substrate	3) Adsorption Steps
		4) Reaction Steps
7) Removal of the Substrate	6) Outward Diffusion of the Substrate	5) Desorption Steps
Substrate Medium	Diffusion Zone	Contact Interface

Individual partial steps can be omitted (e.g., reaction step 4 in pure adsorptions) or can even be combined; the total mechanism is often highly complex. It may not be possible to determine directly the specific role of the contact in question from the resultant kinetics; an example of this is given by the diffusion-determined reactions, which are frequently encountered in applied catalysis. In any case, the reaction proceeds essentially from the specific interaction conditions between the contact and the substrate.

A theory of contact reactions deals primarily with an investigation of the interaction processes. It is basically concerned with the following:

Explaining the action of the contacts on the basis of their material properties.

Deriving the reaction conditions for a given contact-substrate system.

The actual formulation and problematics of the interfacial re-

actions are based on three typical conditions of these processes:

1. The contacts are condensed (usually solid) phases. Their components generally cannot be considered as isolated molecular units; the complex conditions of liquid or solid state physics are much more significant for their properties.

2. The contact particles involved in the interactions are phase-interface atoms. Owing to their unsymmetrical environment, the latter are in special states which differ from those inside the phase. /4

3. Owing to their location at the phase interfaces, the reaction volumes are quasi-two-dimensional. Because their extent in the direction of the surface normals is only molecular, they have a special relationship to the growth reaction volume of a system.

From this we can immediately derive several important facts regarding the chemical properties and surface structure of contacts, as well as the problems involved in investigating heterogeneous reactions.

Surface atoms have unsaturated valences, and therefore have a high chemical activity. Because the surface atoms participate in the contact bond and are subject to anisotropic stress, these valence states differ in principle from those analogous to the corresponding free atoms; as in the case of metals, the chemical properties of contact atoms can be considerably modified.

The interfacial anisotropy affects not only the individual valences, but also the formation of more or less pronounced phase interface layers, which represent certain states. As carriers of space charges, electric potential differences, or even as preferred concentration regions for defects [1], they deserve special consideration in a discussion of contact processes.

In the case of isolated surfaces, particular configurations are found in the phase interface layers. In real surfaces, which are always in contact with the material environment, this gives rise to the possibility of an inducement of properties under the influence of the adjacent medium.

Modification of the bond functions is generally accompanied by changes in the bond intervals. Hence, in the case of interfaces (at least in the outermost atom positions) we must also reckon with special geometrical relationships. These will involve primarily changes in the packing and lattice intervals in the direction of the interface normals. However, it is also necessary to discuss structural changes, especially when a material is in the form of a thin film and is exposed to the (epitaxial) effects of a carrier substrate; these viewpoints deserve special consideration in the theory of carrier contacts. The assumption of a specific surface /5

geometry has recently been undermined by theoretical-computational [3] and experimental [4] studies. [1]

The limited extent of the phase interface states has generally burdened their investigation with particular problems, so that definite facts have thus far been obtained only rarely. Special experimental methods are required for isolated determination of the properties of these atomic layers; electron diffraction could be mentioned as an example. In studying interface reactions, we can use a similar system of problematics for the direct observation of the interaction processes and their molecular representations. Thus far, the IR-investigations developed mainly by Eischens[2] have proved to have the greatest success; recently, however, the methods of microwave spectroscopy have increased in significance [6, 7].

For lack of better knowledge of surface states, contact-chemical studies of the behavior of a contact material are usually based on its volume properties, which are generally critical for its physical and chemical characterization. In such a process, we must always keep in mind the fact that surface and volume states cannot be assumed to be simply identical to one another, so that the conclusions and correlations are based on analogies by assumption.

The difficulties of investigating interfaces (and therefore /6
their precise definition and preparation) lead to the basic experimental problem of the reproducibility and arrangement of contact-chemical measurements, which will be discussed further below (Chapter VI).

How then shall we proceed with the treatment of the basic problem in contact chemistry, namely, determining the interaction relationship of a given contact material and explaining it on the basis of its material structure? We will first discuss the case of a theoretical-deductive procedure.

According to bond theory, a contact is thought of as a giant molecule of finite size, having a three-dimensional lattice, with unsaturated valence functions. The boundary conditions of the finite extent and non-saturation ensure the appearance of the interfacial states.

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[1] As a possible example of this, we can use a silver oxide film studied by electron diffraction, which appears in catalytic H_2O_2 - dissociation in silver (and silver alloys) and under certain conditions in their anodic oxidation as well, and to which none of the previously discussed silver oxide structures can be assigned [2].

[2] The basic work is summarized in [5].

It is clear that the quantum chemical description of such a multi-particle system is much more difficult to formulate than that for a normal molecule. To a much greater extent than in the latter, one must operate with simplifying assumptions and content oneself with rather rough wave-mechanical approximation methods.

The first attempts at calculating the surface states were made by Tamm [8] and Lennard-Jones [9]. Recently, however, there has been a manifestation of increased interest in the quantum chemistry of interfacial systems; in particular, Coulson, Grimley, Huang and Wyllie, Longuet-Higgins, Koutecky and Pollard have made contributions in this regard[3]. Their papers deal primarily with the methodology of the molecular eigenfunctions (MO method).

It is understandable that previous studies have provided information of a general nature, with a lesser amount of concrete data. For practical purposes, semiempirical methods are recommended. Of these, we shall mention only the method of Eley [13] for calculating the heats of adsorption by the Pauling bond formula, since it is at the moment the only discussion with a concrete numerical application. /7

A usable theory of the contact effect should also be suitable for a qualitative operation. For this it seems most advantageous to have a process in which it is attempted to derive the contact behavior of a material from the minimum number of material properties which are of direct significance. At the present state of the art, the nature and influence of such "effective factors" can be determined only on the basis of experimental studies which involve the testing of the correlation possibilities of a comprehensive accumulation of material and discovering regular relationships in it. Suitable methods permit comparison investigations of contact-chemical systems, which show a highly isolated variation of individual system parameters.

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[3] An introduction was recently published by J. Koutecky [10]; another modern survey was provided by T.B. Grimley [11] in an article entitled "The Wave Mechanics of the Surface Bond in Chemisorption". Both articles contain references to the original literature. The reader is also referred to detailed articles in [12].

CHAPTER II

CONTACT EFFECT PARAMETERS

In discussing them as effective factors, we will treat the material properties of a contact as independent and primary determining parameters, regardless of their common origin in a total structure. This view will serve as the basis for the methodological processes and simplifications of a contact theory of the effective factors. /8

The relationships in a contact-substrate system generally result from the interaction of several effective parameters. We know from experience, however, that a simplification is usually possible in this respect; we can limit ourselves to a consideration of individual principal factors, which determine the behavior of a contact system to a considerable extent. The description of the relationships can then be elaborated by adding other factors, finally permiting us to have a very exact representation. At the present time, however, we must content ourselves largely with studying the influence of possible effective factors on the basis of empirical correlations, and establishing concrete relationships in individual cases.

Previous studies of the specificity problem of contacts have led to the formation of the concept of "geometric" and "electronic" factors. These terms involve highly complex concepts. It appears highly justifiable and advantageous to designate two additional basic types by reexamining the concepts involved in the two groups above: these "chemical" or "real structural" factors undoubtedly incorporate individual special cases.

1. GEOMETRIC FACTORS

The boundary surface of a phase is generally composed of regions with different packing or lattice-plane structure. The geometric parameters of the elementary surface types which appear at a contact will be designated here only as geometric factors. According to this definition, other morphological features (grain boundaries, dislocation lines, etc.) are not included among the geometric

factors; the pore structure of a contact is definitely not an effective parameter in this sense, because its influence is not based on the molecular interaction steps.

Historically speaking, geometric concepts constitute the beginning of the theory of contact specificity. /9 We recall the basic research by Balandin [14, 15], whose long years of effort at developing a predominantly geometric concept of catalysis took the form of the so-called multiplet theory. Also important in this respect were the comparison catalytic studies by Beeck et al. [16-19] on the hydration activity of transition metals.

The geometric parameters of a surface type determine its reaction capacity, i.e., the surface density of the possible interaction centers. In this respect, the geometric factors are important in every contact process.

In certain types of reactions, they also play a special role as stereochemical factors. This is the case when the application of the individual substrate molecules at the contact takes place in multicenter bonds or when the elementary reactions involve interactions between (adjacent) chemisorbed substrates. It is easy to see that the mutual stereochemical suitability of the contact and the substrate constitutes a precondition for any interaction of this type, or at least exerts a modifying influence on the bond relationships. Chemisorption bonds, like normal molecular bonds, can be thought of as overlapping states of concrete bond functions; this means that they are essentially localized in certain surface atoms in the contacts, even if changes in the bonds are considerably facilitated energy-wise, and can therefore be confused with delocalized bonds, as in the so-called mobile adsorptions. Hence, the stereochemical relationships influence the energy picture in the individual elementary processes, either by a modification of the bond forces (heats of adsorption) of the chemisorbed reactance or by direct action on the interaction process[4]. Such considerations /10 form the basis for the geometric theories of contact specificity proposed by Balandin, Beeck and others. It must also be mentioned in this regard that the geometric factors constitute only a secondary function, despite their basic significance, even from the standpoint of energy; they determine the intensity, but not the type of contact reaction. Purely geometric contact theories begin, so to speak, half-way: they do not provide an adequate description of the contact-substrate system, because the latter is distinguished primarily by its special chemistry, for which the quantum chemical valence relationships are significant.

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[4] The stereochemical dependence of a reaction energy system has also been studied and determined on a quantum chemical basis, e.g., in calculations of chemisorption of the H_2 molecule; see [20-22].

The stereochemical concepts lead us to expect that different surface types of crystallized contacts will differ in a given case with respect to the interaction process. However, geometric factors are not necessarily always responsible for a "surface specificity"; not infrequently, they are also produced by valence-chemical factors and by anisotropies of the electron properties or of the chemical structure of the different surface types. It may perhaps be possible to gain information regarding this by investigation of test reactions in which purely stereochemical influences are excluded. A suitable reaction appears to be the cathodic dissociation of hydrogen on certain electrode metals, whose measurement on single crystal surfaces is planned.

2. ELECTRONIC AND CHEMICAL FACTORS

The fundamental manner in which a contact enters into an interaction with a substrate is determined by its chemistry. The latter is given in terms of the surface-valence functions based on the quantum-chemical coupling laws of the contact atoms. For the sake of a more precise designation, we can distinguish two cases, using methodology as a criterion, which in our opinion permit a correspondingly objective classification which will allow a significant concretization of the concepts.

In the one case, the interaction properties of a contact are definitely related to certain surface atoms or groups, which also have a highly individual character in the contact and behave in the first approximation like the corresponding isolated species. The interactions with the substrate can be described as normal chemical reactions, in which the contact merely ensures the availability of intermediate reactants. We will call such effective parameters of a contact, "chemical" factors.

Frequently, however, the individuality of the individual contact atoms in a phase bond is concealed to a large extent. The surface atoms in this case are also the carriers of the localized valence functions; however, the latter are also determined and modified to a considerable extent by the collective electron structure of the contact (or its surface region). At least for the present, it seems hardly likely that a conventional chemical designation can be obtained for it; this can be done much more succesfully on the basis of correlations with specific features of the electron structure of a contact, which are manifested in its optical, electrical, and magnetic properties. Here we are speaking of the "electronic" factor. /11

It is mainly the contact substance which determines which type predominates, although the chemical properties of the substrate can also play a role in determining the relationships.

2a. Electronic Factors

The domains for the electronic factor are formed by the metals, alloys, and semiconductors; these classes of materials are distinguished by a delocalization of the critical outer electron states which are clearly expressed in the representational form of the band model (conduction and valence bands).

Fundamental significance was assigned relatively early in heterogeneous catalysis to electronic viewpoints [23-26]; however, these initially consisted only of highly generalized theories. The concepts acquired a more concrete form when Schwab [27-29] was able to show a direct relationship between the catalytic properties and the electronic structure of certain classes of alloys.

The initial discoveries were made with Hume-Rothery alloys [30-31]; the characteristic electronic parameter in this case was the so-called electron concentration, i.e., the relative degree of filling of the conduction bands, according to the theories of Brillouin, Hume-Rothery, and Mott and Jones [32, 33]. Corresponding theories were soon transferred to catalytic investigations of /12
alloys of the subgroup metals with partially unoccupied d-levels ("d-metals") [34-36]. In contrast to the Hume-Rothery alloys, which involved primarily the s-band levels which could be considered separately, the outer electron states of the d-metals and their alloys consisted of overlapping of s- (and occasionnally also p-) bands with the d-bands of the next electron shell inward. This made the relationships somewhat more complex, and it appeared as though the saturation of the d-level was a particularly important parameter, in addition to the general degree of filling of the resulting band.

Occasionally, we also find the so-called "percentual d-character" used as a characteristic parameter for the group of d-metals[5]; this is a concept which stems from the terminology of the Pauling theory of metals [39, 40].

We will not discuss the electronic factor in semiconductor contacts in greater detail, since we will be dealing in the following exclusively with metals and alloys.

The designation of electronic contact factors has still been only slightly differentiated. In addition to the factors which were initially defined by particular theoretical concepts (electron concentration, d-character, etc.), indirectly accessible material properties have also served as characteristic quantities (work function, electrical conductivity, magnetic susceptibility,

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[5] This is found, e.g., in [17, 37]; for a definition of the "percentual d-character", see [38, p. 22 ff].

etc.). The valence-chemical characterization is based on the principle of an acceptor-donor correspondence between the contact and the substrate. In a highly generalized sense, this can be understood as follows: it is based on the mutual tendency to give up or acquire electrons, with no specification of whether covalent bonds or electron transitions are involved in the interaction.

It appears worthwhile to attempt to develop a more concrete concept of the electronic contact factor. In the future, efforts to develop a better representation should deal primarily with the problem of whether it would be possible to obtain a more chemical formulation in the language of the valence theories, for which the band model is less suitable. A starting point for this might be the Pauling theory of metals [39, 40], which involves the concept of the resonance bonds of "hybridized" atom functions rather than the concept of an electron gas, and particularly the "Ligandenfeld" theory. /13

In this respect, we should mention a special problem related to the electronic factor of multicomponent contact materials, such as alloys, to which little attention has been paid in the past; in such systems, owing to the different electron negativities of the components, special inhomogeneities in the surface electron distributions must be taken into account. The latter remain unconsidered in the current system of designation; they must also be taken into account in a valence-chemical concept of the electronic factor.

2b. Chemical Factors

We will forego a systematic discussion for the present, trying instead to develop several fundamental viewpoints for it.

The best example of a chemical contact factor is the functional surface group as the sole interaction carrier of a contact. This case is encountered with a high degree of probability in the oxide contacts of exchange, crack, and dehydration catalyses (SiO_2, Al_2O_2, etc.), where the catalytic function is thought to be exerted primarily by acid groups (surface OH groups); recent papers on this subject are listed in the paper by G. M. Schwab and K. Gossner, entitled "Heterogeneous Catalysis" [41, NB pp. 179 and 196]. The balance of the structure of such contacts does not appear to have any primary significance. It should also be noted that the remaining contacts are bound to the effective group as substituents, and in this capacity can cause different reactivities in the latter.

In many cases, the contact behavior undoubtedly results from the tendency of certain contact atoms to change their valence. The effectiveness of various oxide contacts for catalytic oxidations is probably due to such Redox properties of individual components. In other cases, on the other hand, a difference between the chemical and electronic factors may occur quite formally, namely, in

certain reactions at metal contacts. A closer examination will show, however, that it is generally another problem which is involved here: the determination of whether the elementary contact-substrate interaction is critical for the course of the reaction or whether it is the continued reaction of intermediate bonds, which are viewed as an independent species. In both cases, the designation of the actual contact must be based on its original interaction behavior; in the second case, the total process is characterized much more suitably by the chemical properties of the intermediate bonds concerned. /14

3. FACTORS OF THE REAL STRUCTURE

A real contact always contains packing defects (vacancies, stacking faults, dislocations); if we are dealing with a solid, it is generally subdivided by grain boundaries, and its elementary faces are bounded by edges and corners. It is appropriate to concede these parameters of the real structure, a possible influence on the contact behavior. In heterogeneous catalysis, a critical role was long attributed to the edges and corners of contact crystallites, because the atoms at such excellent positions, in view of their special energy and valence states, serve as preferred activity centers ("adlineation" theory).

The significance of real structural factors has undoubtedly been frequently overestimated. On the other hand, numerous data indicate that they have an influence on the contact behavior; this fact has not yet been explained in detail, particularly with respect to concrete theories regarding the effective mechanisms. In addition, only a few studies have been made thus far which permit definite arrangements to be formed. In general, it appears as though the influence of these parameters was primarily the result of the special relationships in a contact-substrate system and was of highly variable significance from one case to the next.

Real structural characteristics are considered to be the critical parameters for the individual behavior of contacts consisting of materials of the same type, to the extent that this represents true contact characteristics and is not caused by surface impurities and the like. Real structural effects are important primarily in cases of different preparations or special preliminary treatments; we are reminded in this regard of the familar properties of highly disperse contacts and the phenomena of so-called super activity [42].

PART A

THE CONTACT CHEMICAL BASES OF ELECTROLYTIC DISSOCIATION OF HYDROGEN

CHAPTER III

HYDROGEN OVERTENSION

In the next part of this paper, we will limit ourselves to a contact-chemical consideration of an electrode process. It has already been mentioned in the introduction that previous investigations in this regard cannot withstand a detailed examination for various reasons. /15

The object of our studies is the reaction system of the hydrogen electrode. The general designation of "hydrogen overtension" can be used to describe these kinetic phenomena. The hydrogen electrode can be viewed as a fundamental contact system from many aspects.

Because of its special substrate, the various configurations of hydrogen, this electrode has the same significance for adsorption and catalysis as for electrode kinetics. It belongs to the group of electrode systems which have been most investigated from a purely electrochemical and kinetic standpoint [43, 44]; as a main reference electrode, it is deserving of particular interest. Further possibilities for a detailed study of the electrochemical hydrogen reaction were opened up when it became possible to develop a method for its reproducible measurement; this method provides a contact-chemical test system for obtaining reliable and exact findings.

1. THE CATHODIC HYDROGEN DISCHARGE AS A TEST REACTION

The gross reaction of the hydrogen electrode consists of two opposed processes, cathodic hydrogen discharge and anodic hydrogen dissociation:

$$H^+ + e^- \underset{\text{anodic}}{\overset{\text{cathodic}}{\rightleftharpoons}} 1/2\,H_2 .$$

The rates at which the component processes take place are mutually antibatic functions of the impressed electrode polarization; their relationship determines the resultant electrode current. They are equal in amount at equilibrium potential. With sufficiently strong polarization in one direction, the corresponding opposite reaction is negligibly small for the ratio of the rates, independent of special reaction mechanism; we have: /16

$$\frac{V_{anodic}}{V_{cathodic}} \approx \exp\left(\frac{F}{R\,T}\eta\right).$$

where η is the "electrode polarization" or "overtension", i.e., the electrode potential relative to its equilibrium value, (F = Faraday constant, R = gas constant, T = absolute temperature).

Proper selection of the measurement range makes it possible to study the component processes separately and permits a considerable simplification of the discussion. If the contribution of the opposite reaction is below 1%, then for η we have the conditions:

$$\left.\begin{matrix}\eta \\ -\eta\end{matrix}\right\} > \frac{2{,}3\,RT}{F} \cdot 2 \approx 120\ mV \qquad \begin{matrix}\text{(anodic reaction)} \\ \text{(cathodic reaction)}\end{matrix}$$

The investigations described in the present paper deal with the cathodic reaction (η <-120 mV) and (to the extent that special experiments are not involved) particularly with electrodes of the type

Test Contact/2n-sulfuric acid (without conducting salt), because it is precisely this reaction system which appears to be particularly suitable for a treatment of contact-chemical overtension problems.

The cathodic reaction has several advantages over the anodic reaction. Hydrogen dissociation can be studied separately at sufficiently negative polarizations, while simultaneous reactions (at least of the hydrogen electrode) must always be taken into account when the electrode is connected to the anode. In addition, an oxidative reaction with the substrates (formation of a coating on the electrode) are avoided in the cathodic process. In particular, however, dissociation of (base) electrode substances is prevented or suppressed.

When a pure acid is used as the electrolyte, possible side reactions of the cations are also avoided; only water molecules or hydronium ions are involved as reacting substrate particles. Moreover, an acid medium favors the removal of cathode coatings which may originally be present, and prevents formation of genuine metal hydrides, so that the case of a contact reaction with purely chemisorptive interaction conditions is produced with relative certainty. As far as its suitability as a test reaction is concerned, a very important fact is that its kinetics are independent of transport processes or actual interaction steps over a wide range of concentrations and flux densities. /17

It is advantageous to work in the normal case with acid concentrations whose hydrogen ion activity is $a_H = 1$. The selection of a concentration which is not too low is advisable in the absence of a conducting salt, owing to the reduction of the ohmic potential differences in the electrolyte; in particular, however, the relationships are simplified to a considerable degree in another way, because the so-called ζ-potential of the diffuse double layer becomes negligibly small. Especially for a = 1, the experimental findings are directly applicable to the most used reference standard of the standard hydrogen electrode. The unit activity is produced nearly exactly in the 2n-sulfuric acid. The use of sulfuric acid is to be recommended in view of its chemical properties, especially the stability of its anion.

The cathodic hydrogen reaction, like all electrode processes, has important advantages from the standpoint of the measurement method. The principal measured values in a study of the electrode reactions are electrolysis currents and electrode polarizations (overtensions). Currents and potentials can be determined with high accuracy and up to very small amounts without particular difficulty. The electrolysis currents provide a direct indication of the reaction rates, without it being necessary to follow the conversions over a period of time. This makes it possible to determine reaction rates continuously and even at low reactivity with considerable precision. This fact is of considerable importance with respect to work under mild conditions or with small contact surfaces (contact metals, selected preparation).

The correlation of current and polarization yields the "current-potential relationships" of an electrode, whose parameters are determined by the corresponding kinetic and energy relationships of the reaction system. Current-potential relationships constitute the most important information elements in electrokinetic studies.

Electrode currents (I) are usually normalized over the (geometric) unit surface of the electrode and expressed as flux densities (j). /18

A measurable variable of electrode polarization is the overten-

sion η, which can be determined experimentally in contrast to the actual critical absolute potential $\varepsilon(j)$ (at flux density j) as the deviation of the latter

$$\eta = \varepsilon(j) - \bar{\bar{\varepsilon}} = \varepsilon(j) - \varepsilon(0) \quad [6]$$

from the equilibrium value $\bar{\bar{\varepsilon}}$ of the same electrode.

2. REACTION MECHANISMS

2a. Substrate

The cathodically produced hydrogen comes either from hydronium ions or from water molecules:

$$H^+_{aq} + e^- \longrightarrow 1/2\, H_2 \qquad (A)$$

or

$$H_2O + e^- \longrightarrow 1/2\, H_2 + OH^- \qquad (B)$$

H^+_{aq} = hydrated proton (hydronium ion)
e^- = electron from the cathode

For more acid electrolytes and not too high flux densities, we can expect a predominance of hydrogen ion discharge (A). In alkaline media, only the water molecule can contribute to the reaction to a meaningful degree. In general, we must expect an overlap of comparable amounts of (A) and (B).

The pH-dependence of the overtension provides an indication of the relationships. For the pure limiting case, assuming a vanishing ζ-potential (measurements with addition of foreign electrolytes), the following criteria are valid, which can easily be derived from the corresponding kinetic equations [45, 46, 47, 48]:[7] /19

$$\text{pure reaction (A)} \left(\frac{\partial \eta}{\partial \log a}\right)_j = \frac{2{,}3\,RT}{F}\left(\frac{1-\alpha}{\alpha}\right) > 0$$

$$\text{pure reaction (B)} \left(\frac{\partial \eta}{\partial \log a}\right)_j = -\frac{2{,}3\,RT}{F} < 0$$

[6] Unlike the "electrode polarization", overtension is based on individual electrode reactions. If it is only a potential-determining process which is taking place at the elctrode, the polarization and overtension are identical, and the equilibrium potential of the corresponding electrode reaction corresponds to the currentless potential value $\bar{\bar{\varepsilon}} = \varepsilon(0)$. See [44, p. 9].

[7] Somewhat different complex relationships are found when the influence of the foreign electrolyte is considered. See [48,49].

a = hydronium ion activity
α = throughput factor (see Section III, 3)

Qualitative findings of this type permit us to draw some significant conclusions.

An experimental determination of the reacting particles can scarcely be found in the literature, aside from a few special investigations. As representative examples of the types of cathodes used in this work, we therefore investigated copper and gold, as well as a few of the alloys which differ most markedly in their overtension behavior from the original metal (Cu-Ga III, Au-In II) at three acid concentrations. Characteristic overtension values from the current-potential curves which were obtained are listed in Table I and plotted in Figure 1 as a function of the hydrogen-ion activities.

The values of the throughput factors all lie within $\alpha = 0.55 \pm 0.01$. The pH-values of the mixed electrolytes, listed in the table under (a), were calculated from our own measurements of the reversible chains

$$\text{Pt}(H_2) \;\Big|\; \begin{matrix} x\,\text{m}\ H_2SO_4 \\ 1\,\text{m}\ (NH_4)_2SO_4 \end{matrix} \;\Big|\; \text{calomel electrode}$$

The values given by Barnartt [50, 51] for pure acids are listed under (b).

TABLE I. OVERTENSION VALUES FOR DETERMINING HYDROGEN-PRODUCING REACTANTS /20

(flux density $j = 10\ \text{mA/cm}^2$; $T = 20^0\text{C}$)

electrolyte	pH		$-\eta_{10}$ (mV)			
	a	b	Cu	Cu-Ga III	Au	Au-In II
1m H_2SO_4		0,05	551	575	395	390
1m H_2SO_4 + 1m $(NH_4)_2SO_4$	0,26	0,05	574	589	405	415
0,1m H_2SO_4 + 1m $(NH_4)_2SO_4$	1,52	1,10	612	633	440	458
0,01m H_2SO_4 + 1m $(NH_4)_2SO_4$	2,58	1,86	580	623	450	425

The results show that at higher acid concentrations, the hydronium ion causes the reaction ($\partial\eta/\partial \log a > 0$) in all cases; for this range, it is also possible to determine a good qualitative agreement of the experimental pH-dependence with the theoretical pH-dependence which would be expected in the case of a pure proton reaction. The transition which takes place at smaller acid concentrations will not be discussed here.

2b. Elementary Reactions

For the reaction

$$2(H^+_{aq} + e^-) \longrightarrow H_2$$

which is significant only in highly acid media, the elementary steps summarized in the following diagram will be discussed.

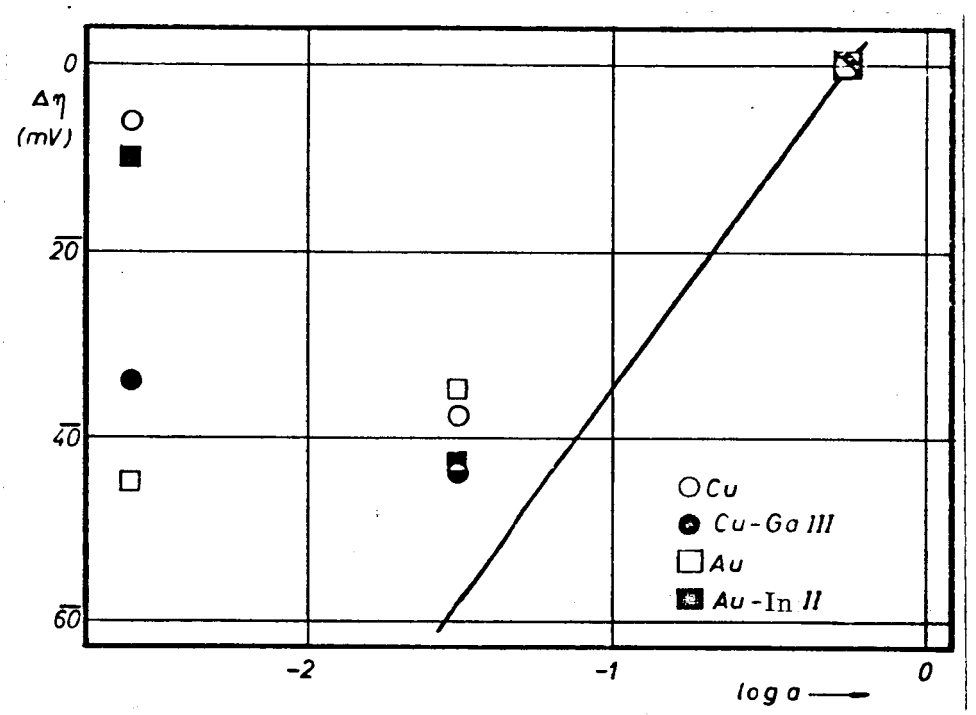
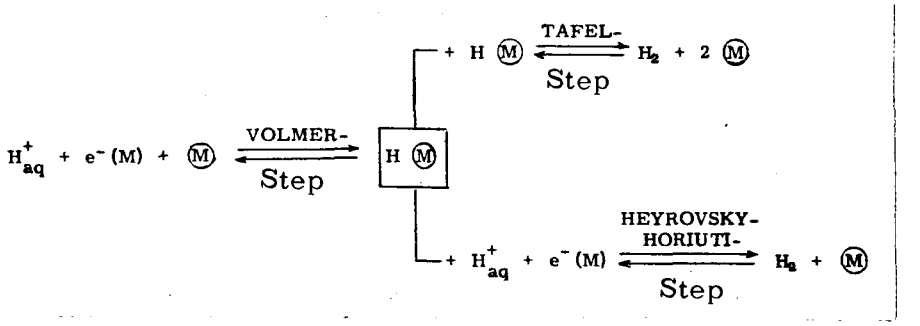


Fig. 1. pH-Dependence of Hydrogen Overtension with Addition of Conducting Salt $\Delta\eta = \eta$ (xm - H_2SO_4) - η (1 m - H_2SO_4). The Line Corresponds to the Simple Frumkin Formula for Hydrogen Extraction from Hydronium Ions.

A proton is initially discharged in the Volmer step and adsorbed as a hydrogen atom on the surface of the cathode. Ensuing formation of the molecular hydrogen then takes place either in the Tafel step by combination of two such adsorbed atoms or in the Heyrovsky-Horiuti step by interaction with another proton of the electrolyte, in which case a discharge process ("throughput reaction") /21



H^+_{aq} = hydronium ion
$e^-(M)$ = electron from cathode metal M
Ⓜ = free adsorption site of cathode metal M
H Ⓜ = hydrogen atoms adsorbed on cathode metal M.

takes place in the next step. A reaction without actual adsorption steps, in which two protons are discharged and combined in the field of the electrode double layer, is improbable; it would be viewed as the limiting case of the above mechanisms.

The elementary steps presuppose transport processes in the electrolytes, which need not be considered here. Likewise, the intermediate steps of the molecularly adsorbed hydrogen have been omitted as unimportant under the reaction conditions given above.

The rate equations for the cathodic forward reactions of the elementary steps are written as follows: /22

$$v_V = k_V \underline{a}(1-\vartheta)\exp\left(-\frac{\Delta G_V^{\ddagger}}{RT}\right)$$

$$v_T = k_T \vartheta^2 \exp\left(-\frac{\Delta G_T^{\ddagger}}{RT}\right)$$

$$v_H = k_H \underline{a}\,\vartheta \exp\left(-\frac{\Delta G_H^{\ddagger}}{RT}\right)$$

Here, v_V, v_T, v_H are the reaction rates; k_V, k_T, k_H are the frequency factors[8] and $\Delta G_V^{\pm}$, $\Delta G_T^{\pm}$, $\Delta G_H^{\pm}$ are the free activation enthal-

[8] See Chapter V.2, however.

pies of the Volmer, Tafel, and Horiuti reactions. a is the hydrogen ion activity at the double layer boundary, and ϑ represents the degree of occupation of the adsorption sites available on the cathode surface [$(1-\vartheta)$ = fraction of free sites].

From the expressions for the (anodic) reverse reactions, let us write only the one for the Volmer steps which will be required later on:

$$v_{aV} = k_{aV}\,\vartheta \exp\left(-\frac{\Delta G^{\ddagger}_{aV}}{RT}\right).$$

2c. Potential Dependence

The potential dependence of the reaction rates is found from those free activation enthalpies of the throughput step, which can enter both directly into the Arrhenius term and implicitly into the kinetic equations above a degree of coverage ϑ. The reaction energy diagrams in Figure 2 show the enthalpy-potential relationships. The critical electrical potentials are (1) the potential ϕ_K within the contacts, (2) the potential ϕ_E at the double layer boundary of the electrolytes and (3) the potential $\phi^{\ddagger}$ at the site of the activated reaction complex. The electrode potential of the reaction layer

$$\underline{\varepsilon} \equiv \varphi_K - \underline{\varphi_E}$$

differs from the "absolute potential" of the electrode, relative to the interior of the electrolyte according to the definition: /23

$$\varepsilon \equiv \varphi_K - \varphi_E = \varphi_K - \underline{\varphi_E} + \zeta$$

by the value of the ζ-potential.

At electrode potential $\underline{\varepsilon} = 0$, the free activation enthalpy of the cathodic reaction steps is:

$$\Delta G^{\ddagger} = G^{\ddagger} - \underline{G},$$

while that of the anodic is:

$$\Delta G^{\ddagger}_{a} = G^{\ddagger} - G_p,$$

where $\underline{G}$, $G^{\ddagger}$ and G_p are the free enthalpies of the system in the initial state, in the activated complex, and in the product state. If ε becomes nonzero, the free enthalpies of the states containing charged particles change their amounts of electrical energy. Since the potential at the electrolyte boundary has shifted according to the definition $\underline{\varepsilon} \equiv \phi_K - \phi_{\underline{E}}$ by the full amount $-\varepsilon$ and at the

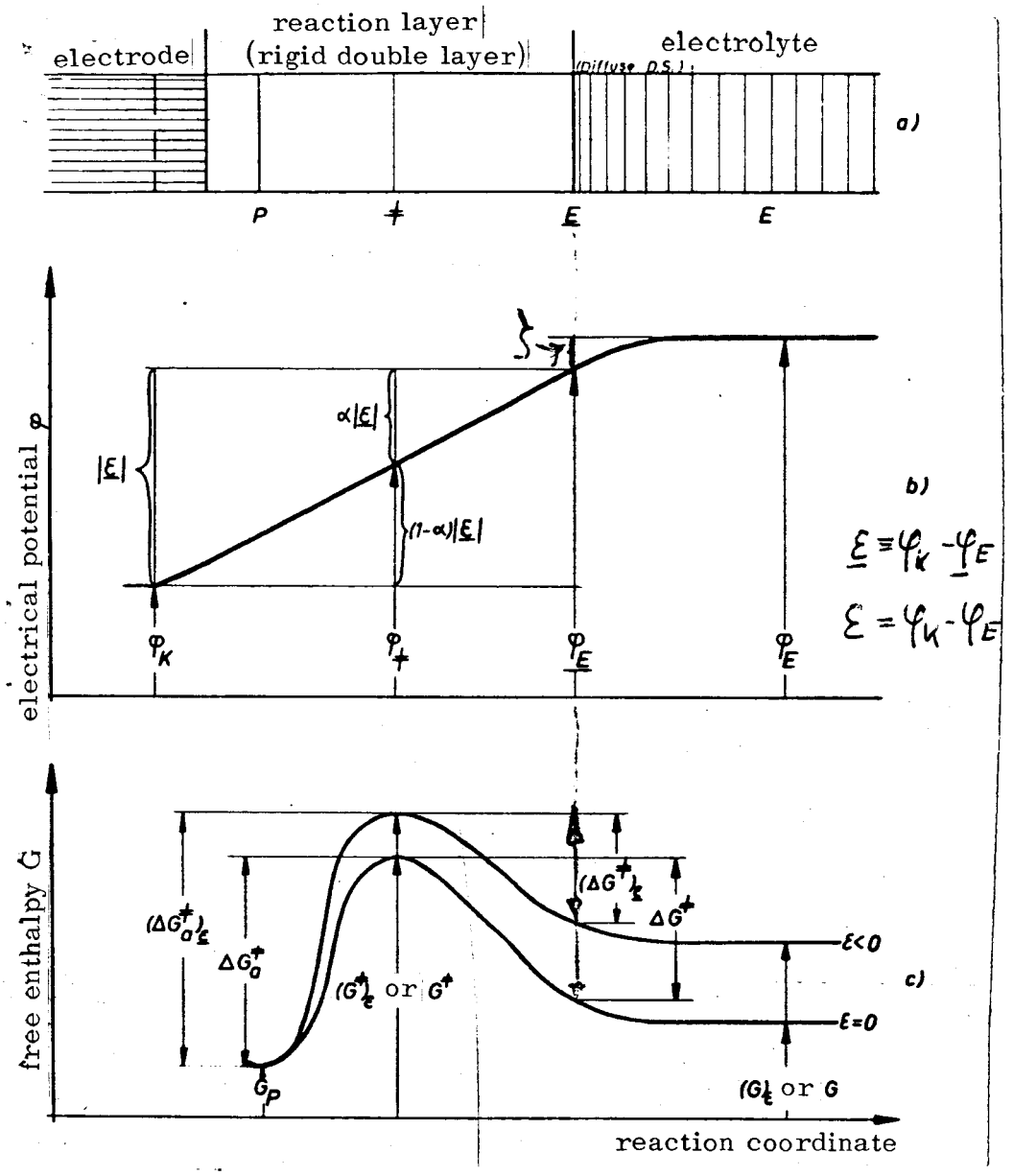


Fig. 2. Pattern and Energy Relationships in a Throughput Reaction. (a) Topographic Diagram. (b) Potential Relationships (Simplified) for $\varepsilon < 0$. (c) Reaction Energy Profile.

site of the activated complex by the fraction $-(1-\alpha)\varepsilon$, we now have the following equations which are valid for the (molar) enthalpies (z = charge number):

$$(\underline{G})_{\underline{\varepsilon}} = \underline{G} \pm zF\underline{\varepsilon}$$

$$(G^{\ddagger})_{\underline{\varepsilon}} = G^{\ddagger} - (1-\alpha)\, zF\underline{\varepsilon}$$

$$(G_P)_{\underline{\varepsilon}} = G_P .$$

For the activation enthalpies, we obtain (with z = 1 for the hydrogen reaction):

$$(\Delta G^{\ddagger})_{\underline{\varepsilon}} = \Delta G^{\ddagger} + \alpha F \underline{\varepsilon}$$

$$(\Delta G_a^{\ddagger})_{\underline{\varepsilon}} = \Delta G_a^{\ddagger} - (1-\alpha) F \underline{\varepsilon}$$

The "throughput factor" α is known to be constant over wide ranges of polarizations; its value lies in the vicinity of 0.5.

The $\Delta G^{\pm}$ and $\Delta G_a^{\pm}$ (for $\underline{\varepsilon} = 0$) are usually referred to as the "purely chemical" activation enthalpies, which have only a formal significance. Such a concept appears inaccurate for two reasons: /24

1. These values are not formally defined, but are the actual activation enthalpies $(\Delta G^{\pm})_{\underline{\varepsilon}}$ at the special polarization $\underline{\varepsilon} = 0$.

2. In general, they do not represent any purely chemical values, since the latter would also require $\phi^{\pm} = \underline{\phi_E}$ as well as $\phi_K = \underline{\phi_E}$. This is not necessarily the case, however, as we can see from a consideration of the buildup of potential on electrodes with dipole adsorption; an energy component produced by $\phi^{\pm} - \underline{\phi_E}$ or $\phi^{\pm} - \phi_K$ at $\phi_K = \underline{\phi_E}$ is already contained in $\Delta G^{\pm}$ or $\Delta G_a^{\pm}$.

3. CURRENT-POTENTIAL RELATIONSHIPS

The rate equation of the reaction is obtained from the kinetic equation of one of its elementary steps by introducing an explicit expression for ϑ. The latter is provided by the immobility condition for the corresponding mechanism. Using the flux density as a rate value, the kinetics are obtained in the form of a current-potential relationship.

If a single elementary step determines the kinetics, the current-potential relationship assumes the particularly simple form of the familiar Tafel equation. We will clarify the relationships briefly for the possibilities of a "reaction-determining" Volmer or Horiuti step which occurred in our investigations alone. For this we can use a consideration of the Volmer-Horiuti mechanism, although the latter does not cover all cases owing to its definition condition: $V_T \ll V_H$. The immobility relationship of the Volmer-Horiuti mechanism

$$V_V - V_{aV} - V_H = 0$$

gives us liefert $\left(k' = k \exp\left(-\frac{\Delta G^{\ddagger}}{RT}\right)\right)$,

$$\vartheta = \frac{k'_V \underline{a} \exp\left(-\alpha_V \frac{F}{RT}\underline{\varepsilon}\right)}{k'_V \underline{a} \exp\left(-\alpha_V \frac{F}{RT}\underline{\varepsilon}\right) + k'_{aV} \exp\left((1-\alpha_V)\frac{F}{RT}\underline{\varepsilon}\right) + k'_H \underline{a} \exp\left(-\alpha_H \frac{F}{RT}\underline{\varepsilon}\right)}$$

and by introducing this expression into $j = 2F \cdot V_H$ we obtain /25

$$j = 2F \frac{k'_V k'_H \underline{a}^2 \exp\left(-\alpha_V \frac{F}{RT}\underline{\varepsilon}\right) \exp\left(-\alpha_H \frac{F}{RT}\underline{\varepsilon}\right)}{k'_V \underline{a} \exp\left(-\alpha_V \frac{F}{RT}\underline{\varepsilon}\right) + k'_{aV} \exp\left((1-\alpha_V)\frac{F}{RT}\underline{\varepsilon}\right) + k'_H \underline{a} \exp\left(-\alpha_H \frac{F}{RT}\underline{\varepsilon}\right)}$$

as the general current-potential equation.

Now if (1)

$$\frac{V_H}{\vartheta} \gg \frac{V_V}{\vartheta} + \frac{V_{aV}}{\vartheta} \quad ,$$

we will have

$$\vartheta = \frac{k'_V \exp\left(-\alpha_V \frac{F}{RT}\underline{\varepsilon}\right)}{k'_H \exp\left(-\alpha_H \frac{F}{RT}\underline{\varepsilon}\right)} \approx 0$$

and

$$j = 2F k'_V \underline{a} \exp\left(-\alpha_V \frac{F}{RT}\underline{\varepsilon}\right)$$

for a reaction-determining Volmer step.

With $\frac{V_V}{\vartheta} + \frac{V_{aV}}{\vartheta} >> \frac{V_H}{\vartheta}$, i.e., a reaction-determining Horiuti step, there are two cases to be discussed:

IIa) $\frac{V_V}{\vartheta} \gg \frac{V_{aV}}{\vartheta} + \frac{V_H}{\vartheta}$

$$\vartheta = \left(\frac{k'_V \underline{a} \exp\left(-\alpha_V \frac{F}{RT}\underline{\varepsilon}\right)}{k'_V \underline{a} \exp\left(-\alpha_V \frac{F}{RT}\underline{\varepsilon}\right)}\right) = 1$$

$$j = 2F k'_H \underline{a} \exp\left(-\alpha_H \frac{F}{RT}\underline{\varepsilon}\right)$$

IIb) $\frac{V_{aV}}{\vartheta} \gg \frac{V_V}{\vartheta} + \frac{V_H}{\vartheta}$

$$\vartheta = \frac{k'_V \underline{a}}{k'_{aV} \exp\left(\frac{F}{RT}\underline{\varepsilon}\right)} = \vartheta(\underline{a}, \underline{\varepsilon}) \quad \begin{matrix} < 1 \\ > 0 \end{matrix}$$

$$j = 2F \frac{k'_V k'_H}{k'_{aV}} \underline{a}^2 \exp\left(-(1+\alpha_H)\frac{F}{RT}\underline{\varepsilon}\right) .$$

For these as for all other boundary cases, we therefore always find a simple exponential dependence

$$j = j_0 \exp\left(-\frac{2,3}{b}\underline{\varepsilon}\right)$$

of the flux density upon the electrode potential. If we replace $\underline{\varepsilon}$ in the above by the measured variable, the overtension $\eta \equiv \varepsilon - \bar{\varepsilon}$ [9], and select the logarithmic form, we obtain the Tafel equation

$$\eta = a_T - b \log j$$

with $a_T \equiv b \log j_0$;

$$j_0 \equiv 2F k'_V \underline{a} \exp\left(-\alpha_V \frac{F}{RT}\bar{\varepsilon}\right)$$

for a reaction determined by the Volmer step and

$$j_0 \equiv 2F k'_H \underline{a} \exp\left(-\alpha_H \frac{F}{RT}\bar{\varepsilon}\right) \quad \text{(Case IIa)}$$

---

[9] For the sake of clarity, we have assumed here that $\zeta(\varepsilon)$ and $\zeta(0) = 0$.

or

$$\equiv 2F \frac{k'_V k'_H}{k'_{aV}} \underline{a}^2 \exp\left(-(1+\alpha_H)\frac{F}{RT}\bar{\varepsilon}\right) \quad \text{(Case IIb)}$$

for a determining Horiuti step.

We will call the value j_0 the "effective exchange flux density", since (strictly speaking) it is not identical to the "exchange flux density" $\bar{j}_0$ defined for the state at equilibrium potential, but rather is based on the conditions in the range of validity of the corresponding Tafel equation. /27

The Tafel constants a_T and b and therefore j_0 can be obtained from the experimental Tafel curves. The slopes b allow us to obtain definite information regarding the reaction mechanism, as we can see from Table II.

TABLE II. TAFEL b-VALUES AND MECHANISMS OF HYDROGEN DISSOCIATION

$b = \beta \frac{2{,}3\,RT}{F}$ (mV)		degree of coverage ϑ	mechanism	corresponding step
β	b for $\alpha = 0{,}5$, $T = 20^0C$			
$\frac{1}{2}$	29	$0 < \vartheta(\underline{a}, \eta) < 1$	VOLMER-TAFEL	T
$\frac{1}{1+\alpha_H}$	38	"	VOLMER-HORIUTI	H (case IIb)
$\frac{1}{\alpha_V}$	116	"	VOLMER-TAFEL	V
"	"	≈ 0	VOLMER-HORIUTI	V
$\frac{1}{\alpha_H}$	"	≈ 1		H (case IIa)
[	∞	≈ 1	VOLMER-TAFEL	T (limiting current)]

The a_T or log j_0-terms contain the information on the interaction relationships in the contact-chemical elementary steps. Their exact representation in explicit form will be given in Chapter V following a required analysis of the experimental and theoretical potential relationships.

CHAPTER IV

ELECTRODE POTENTIALS

The measurement of electrode potentials is always a measurement of cell voltages. The cell voltage (E) is the resultant potential difference composed of the various individual potential differences of the corresponding measurement circuit; one of these is the absolute potential ε_M of the test electrode K(M). In a contact-chemical discussion of an electrode and especially in the corresponding comparative investigations of various electrode-contact systems, the potential relationships in the measurement circuit must always be taken into account precisely, since it is not E but the absolute potential of the reaction layer ε_M which enters into the contact-chemical values (e.g., j_0). Previous literature in this regard has dealt exclusively with inadmissible assumptions; with regard to the potential relationships, it generally offers a completely confused picture of contradictory theories. /28

In the following consideration, it is assumed that the ohmic potential differences, which are not electrode-specific, are eliminated from the portion of the measurement circuit through which the current has flowed. For the sake of clarity, the ζ-potential will be disregarded at first.

1. CIRCUIT ARRANGEMENT

The potential of a test electrode can be determined relative to the opposite electrode (in our case, the anode) of the electrolysis cell or a reference electrode which is not involved in the current transport. A prerequisite for the above method is the constancy (non-polarizability) of the opposite electrode, i.e., the independence of its potential from the experimental variables; it appears questionable whether this condition can be ensured. Hence, in our investigations we always used the method with the reference electrode, in which the current and potential measurement circuits are widely separated. The circuit diagram is shown in Figure 3. For direct measurement of the overtension and avoidance of diffusion potentials, one of the test electrodes was selected for use as the corresponding reference electrode and exposed to the same electrolyte (platinum $Pt(H_2)$/test electrolyte). The reference electrode is connected to the electrolysis cell by a Luggin lifter.

No resistance elements (measurement instruments, etc.), with the exception of the negligible line resistance, are connected between the grounding point E and the test cathode K.

2. MEASUREMENT CIRCUIT POTENTIALS /29

The conducting elements of the measurement circuit and their potential relationships (chosen arbitrarily with respect to direction and magnitude) are shown in detail in Figure 4. As the cathodic conducting metal, we have indicated that of the reference electrode, since the other metal/metal-potentials in the measurement circuit compensate one another (at the same temperature).

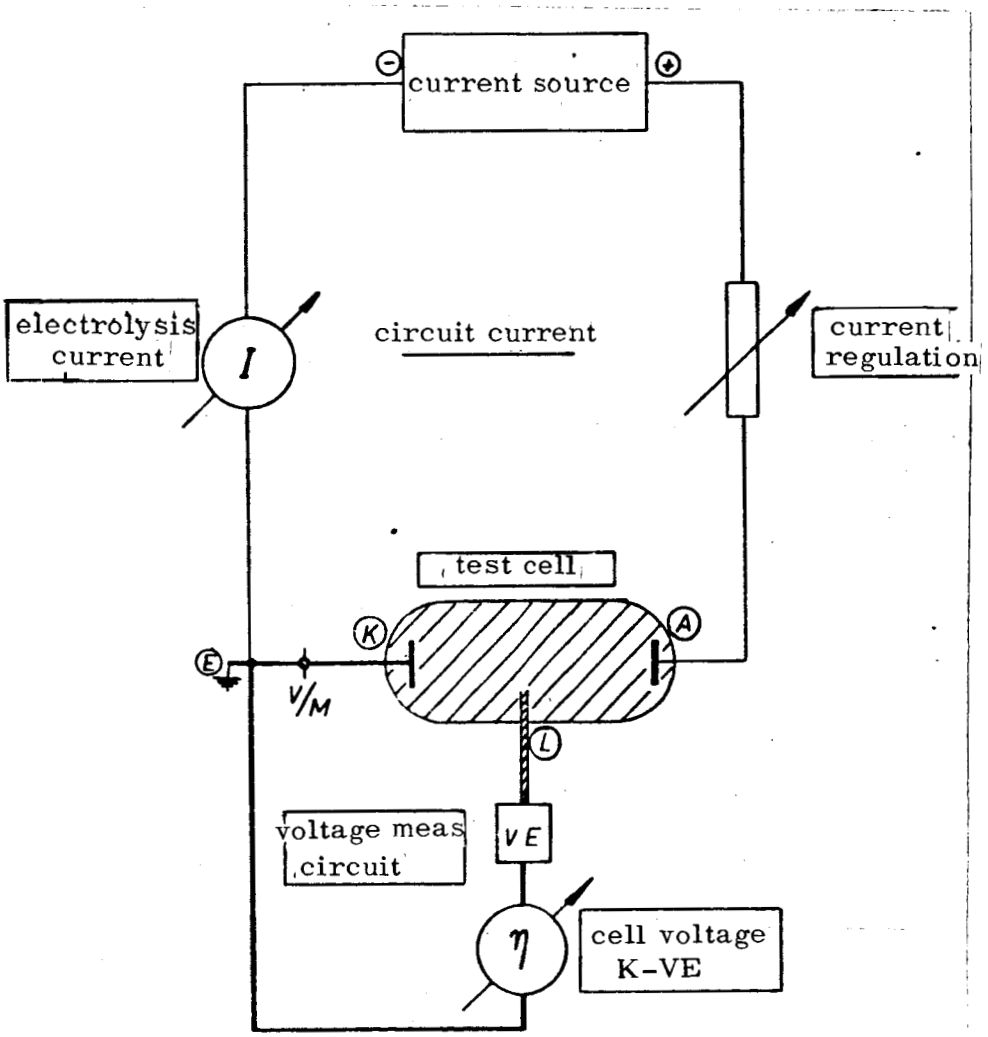


Fig. 3. Circuit Diagram for Cathodic Overtension Measurement. A = Anode; E = Ground; K = Test Cathode; L = Luggin Lifter; VE = Reference Electrode; V/M = Contact Between Cathode Metal M and Measurement Circuit Line V.

The following potential differences appear:

$(\varphi_V)_1 - \varphi_M \equiv \kappa_{VM}$	Contact potential reference metal V/cathode metal M
$\varphi_M - \varphi_E \equiv \varepsilon_{ME}(j)$	Absolute potential of the test electrode
$(\varphi_V)_2 - \varphi_E \equiv \bar{\bar{\varepsilon}}_{VE}$	Reverse absolute potential of the reference electrode

Their algebraic sum gives the overtension (= cell potential)

$$\sum \Delta\varphi_{xy} = (\varphi_V)_1 - (\varphi_V)_2 \equiv \kappa_{VM} + \varepsilon_{ME}(j) - \bar{\bar{\varepsilon}}_{VE} = \eta(j)$$

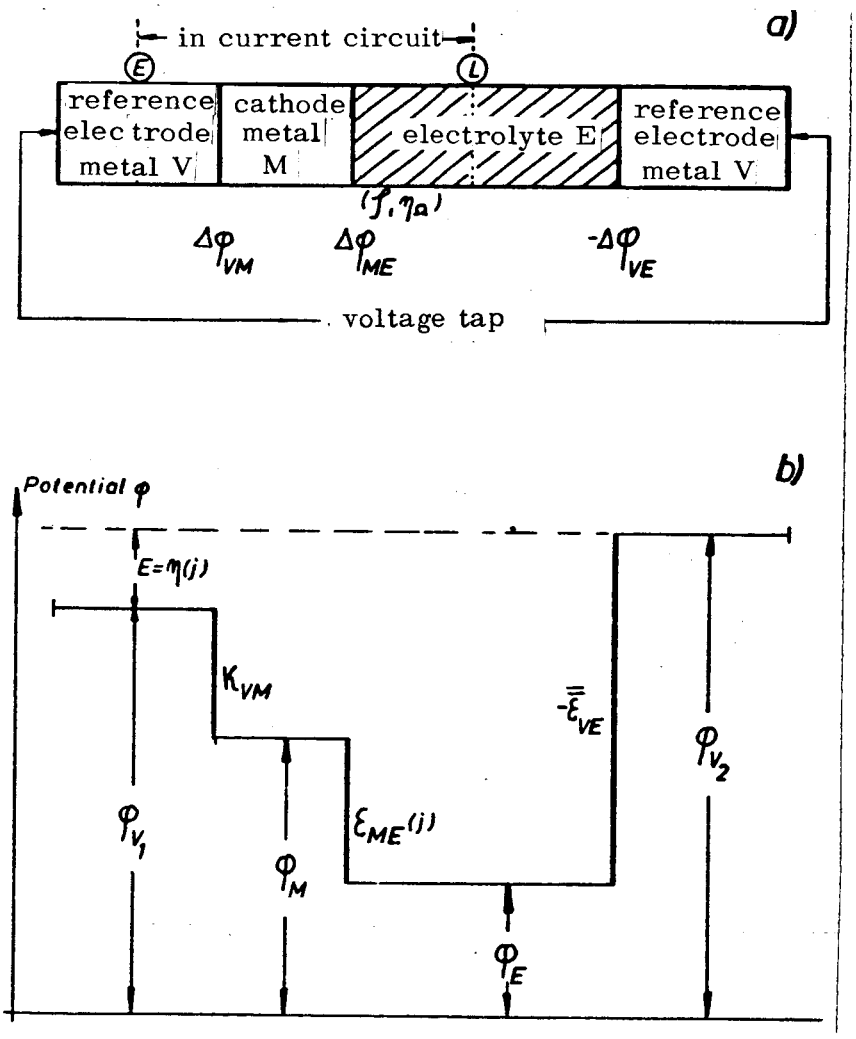


Fig. 4. Potentials in the Overtension Measurement Circuit. (a) Topographic Diagram; (b) Potential Profile (Schematic).

and for $\eta = 0$ we have the relationship

$$\bar{\bar{\varepsilon}}_{ME} - \bar{\bar{\varepsilon}}_{VE} + \kappa_{VM} = 0$$

between the equilibrium potentials. The equilibrium potential $\bar{\bar{\varepsilon}}_{ME}$ of the test electrode, used in the substitution of the overtension for the reaction-kinetic critical potential

$$\varepsilon_{ME}(j) = \eta(j) + \bar{\bar{\varepsilon}}_{VE} - \kappa_{VM}$$

$$= \eta(j) + \bar{\bar{\varepsilon}}_{ME}$$

in the equilibrium equations, is therefore a function of the cathode material.

We see from the above that in all comparison studies of the contact behavior, we must take into consideration the principle of the contact potentials as well as the work functions Φ of the electrode metals to be compared, which are given by /30

$$\kappa_{M_1M_2} = -\frac{1}{e_0}(\Phi_{M_1} - \Phi_{M_2})$$

(e_0 = elementary charge)

it strikes one as surprising that this fact has not been considered in the detailed studies, although it was shown a long time ago in the case of the thermodynamic treatment of reversible chains [52] that the potential sums must contain the contact potentials. Even in special studies [37] of the correlation of the overtension process with the work function of an electrode metal, this relationship is mentioned only with respect to a possible dependence of the heats of adsorption of atomic hydrogen ($H_{(M)}$), without any mention of the involvement of the work function over the $\bar{\varepsilon}_{ME}$ in the values (j_0). A thorough search of the literature revealed only two papers [53, 54] in which the potential relationships were discussed in a manner similar to ours; however, no conclusions were drawn regarding the consequences for the kinetic formulations or were obscured by overly specialized assumptions and omissions.

The reason for this lack of clarity may be found in the fact that the influence of the electrode material is not manifested in cell voltage measurements, because the absolute potentials differ to a degree which depends on the values of the corresponding contact potentials. Such a compensation corresponds to the thermodynamic definition of the cell voltage, which is independent of the electrode material, being a function of the free reaction enthalpy ($\Delta G = nFE$) of the growth cell reaction for Redox systems. This means that even in the case of single electrodes we can assume uniform potential values for a given electrode process. To reduce

errors of this kind, these relationships should be treated in an explicit form in the classroom and in the textbooks.

The altered potential relationships of a given single electrode /31

$$\bar{\bar{\varepsilon}}_{M_1E} + \frac{\Phi_{M_1}}{e_0} = \bar{\bar{\varepsilon}}_{M_2E} + \frac{\Phi_{M_2}}{e_0} = \ldots\ldots = C_E$$

offer, by special combinations, independent expressions for the electrode potentials

$$\bar{\bar{\varepsilon}}_{ME} = C_E - \frac{\Phi_M}{e_0}$$

with a term $-\Phi_M/e_0$ which describes the influence of the electrode material, and a term C_E which is universal for the given reaction conditions.

A comparison of this term sum with one which results from the discussion of a circuit process also leads to a perhaps not uninteresting relationship between the metal surface potentials χ_M and the Peltier heats or reaction entropies. According to Strehlow [55], e.g., the absolute potential of the hydrogen electrode is:

$$\bar{\bar{\varepsilon}}_{ME} = \frac{1/2\,D + H_H - H_{H^+} + I_H}{F} - \frac{T\Delta S_{ME}}{F} + \chi_M - \frac{\Phi_M}{e_0}$$

D = Dissociation energy of the hydrogen molecule.
H_H, IH = Hydration and ionization energies of atomic hydrogen.
H_{H^+} = Hydration energy of the proton.
$-T\Delta S_{ME}$ = Peltier heats (entropy balance of the electrode reaction).

Because

$$\frac{1/2\,D + H_H - H_{H^+} + I_H}{F} - \frac{T\Delta S_{ME}}{F} + \chi_M \equiv C_E + f(M)$$

and

$$\frac{1/2\,D + H_H - H_{H^+} + I_H}{F} + f(M)$$

we therefore also have

$$\chi_M - \frac{T\Delta S_{ME}}{F} \equiv \text{const} + f(M);$$

i.e., the sum of the surface potential and the Peltier heats is independent of the material; although we will not discuss the matter further here, this results in a direct relationship between χ and the reaction entropy of the charge throughput at the metal surface.

3. ζ-POTENTIAL. REACTION KINETICS WITH REGARD TO HYDROGEN ION CONCENTRATION

/32

We know that in the general case of a reaction boundary layer (rigid Helm-holtz layer), a diffuse electrolyte layer (Gouy-Chapman layer) is formed in contact with the electrolyte, in which the reactant concentrations gradually change from their volume value to a kinetically critical boundary layer value. The decrease in the concentration of the charged reactants leads to the formation of the ζ-potential

$$\zeta = \underline{\varphi_E} - \varphi_E .$$

The ζ-potential is the characteristic value of the diffuse double layer; it determines the deviations of the boundary layer parameters $\underline{a}$ and $\underline{\varepsilon}$ from their volume values:

$$\underline{a} = a \exp\left(-\frac{zF}{RT}\zeta\right)$$

$$\underline{\varepsilon} = \varepsilon - \zeta$$

(z ▫ charge number; $z_{H_3O^+}$ ▫ +1).

Following substitution of the volume values which are critical in the experiment for $\underline{a}$ and $\underline{\varepsilon}$, the rate equations read as follows:

$$j = 2F\, k'a \exp\left(-\frac{\alpha F}{RT}\bar{\varepsilon}\right) \exp\left(-\frac{(1-\alpha)F}{RT}\zeta\right) \exp\left(-\frac{\alpha F}{RT}\eta\right).$$

The ζ-potential is therefore introduced into the kinetic characteristic value j_0. It is therefore absolutely necessary to determine its value in evaluations of j_0 or in comparison studies, or at least to ensure uniform conditions for the comparison system[10].

The ζ-potential depends on the electrolyte composition, especially the concentration of the reactants (hydrogen ions) and the electrode polarization and overtension; studies of pH and salt effects provide an indication of its value; their polarization dependence causes definite changes in the throughput factors.

3a. Relationships on Copper and Gold Cathodes

/33

From the rate equations, we have [45]:

$$\left(\frac{\partial \eta}{\partial \ln a}\right)_j = \frac{1-\alpha}{\alpha}\left(\frac{RT}{F} - \left(\frac{\partial \zeta}{\partial \ln a}\right)_j\right)$$

[10] No attention has been given to these assumptions in the past.

TABLE III. pH-DEPENDENCE OF THE OVERTENSION PARAMETERS OF GOLD AND COPPER

(Pure Sulfuric Acid Without Addition of Conducting Salt; T = 21° C)

$[H_2SO_4]$(mol/l)	$-a_T$ (mV)	b (mV)	α	$-\log j_0$
a) Gold				
0,01	600 ± 2	103 ± 1	0,569	5,83 ± 0.03
0,1	595 5	103,5 1	566	5,75 0.03
1,0	603 3	103 0,5	569	5,86 0.04
2,0	589 3	102 1	577	5,81 0.04
3,0	578 2	100 1	586	5,78 0.04
5,0	565 3	99 1	592	5,71 0.03
8,0	550 4	98 1	598	5,61 0.04
12,0	526 3	96 1,5	610	5,48 0.04
b) Copper (informative measurements)				
0,01	776	108	0,540	7,20
0,1	775	107	544	7,25
1,0	765	105	555	7,25
1,5	767	110	530	6,97
3,0	755	108	540	7,00
5,0	736	109	534	6,75

TABLE IV. pH-DEPENDENCE AND ζ-LIMITS OF CATHODIC HYDROGEN DISSOCIATION FROM ACIDS

electrode system	conc. range in which $\frac{\partial \eta}{\partial \ln a_{H^+}} = 0$	literature
Pb/H_2SO_4	0,1n - 8n	KABANOW u. JOFA [56]
Hg/HCl	0,001n - 1,0n	HERASYMENKO u. SLENDYK [57] LEWINA u. SARINSKY [58] JOFA u. FRUMKIN [59-61] BOCKRIS u. PARSONS [62]
Ni/HCl	0,0003n - 0,003n	LUKOWZEW, LEWINA u. FRUMKIN [63] LEGRAN u. LEWINA [64]
Ag/HCl	0,001n - 0,01n	BOCKRIS u. CONWAY [65]
Cu/H_2SO_4	0,02n - 2n	this paper
Au/H_2SO_4	0,02n - 2n	

for the pH-dependence of the overtension. According to [45], since the double layer for pure acids is

$$\zeta \approx \text{const} + \frac{RT}{F} \ln a$$

according to the Stern theory, the overtension should be independent of concentration for $\zeta \neq 0$ and, as soon as ζ becomes zero, it should become more positive with the slope

$$\left(\frac{1-\alpha}{\alpha}\right) \frac{RT}{F}$$

We investigated the pH-dependence of the hydrogen overtension for our basic metals, copper and gold, using pure sulfuric acid as the electrolyte. The results are shown in Table III and in Figures 5 and 6; they were obtained on the basis of experimental Tafel lines, plotted according to the abrasion method (cf. Chapter VI). It is primarily the sulfuric acid concentration which serves as a measure of the concentration, because the hydrogen ion activities are known less exactly or not at all (in the case of high acid concentrations).

In the experiments with 12m sulfuric acid, the plexiglas and araldite cathode holders showed white coatings after the electrolyte was rinsed away with distilled water. It may be that the attack on the holder material had already begun during the tests, so that these measurement data may possibly have been falsified to a certain degree by impurities from products of the composition.

We can draw the following conclusions from the experimental results:

(1) For hydrogen ion activities below a value of $a \approx 1$, the overtension is independent of concentration. Above $a \blacksquare 1$, the overtension becomes more positive, with a slope which is not given exactly due to the lack of activity values, but is obviously in very good agreement with the values required by theory. This means that the experiments completely confirm the Frumkin formula for a first order reaction kinetics in terms of the hydrogen ion activity. In accordance with the b-values obtained, this means that the Volmer step or the Horiuti step (mechanism IIa) determines the kinetics for this experimental system over a wide range of concentrations. /35

(2) The ζ-limit, at which ζ becomes zero, is almost exactly at the hydrogen ion activity $a = 1$. Therefore, in the studies with 2n-sulfuric acid, we can use the simplified formulas for $\zeta = 0$ with $\underline{a} = a$ and $\underline{\varepsilon} \blacksquare \varepsilon$.

(3) In both cases (copper and gold), the ζ-potential vanishes at approximately the same acid concentration. One might be tempted to view this finding as being generally valid (for pure acids and

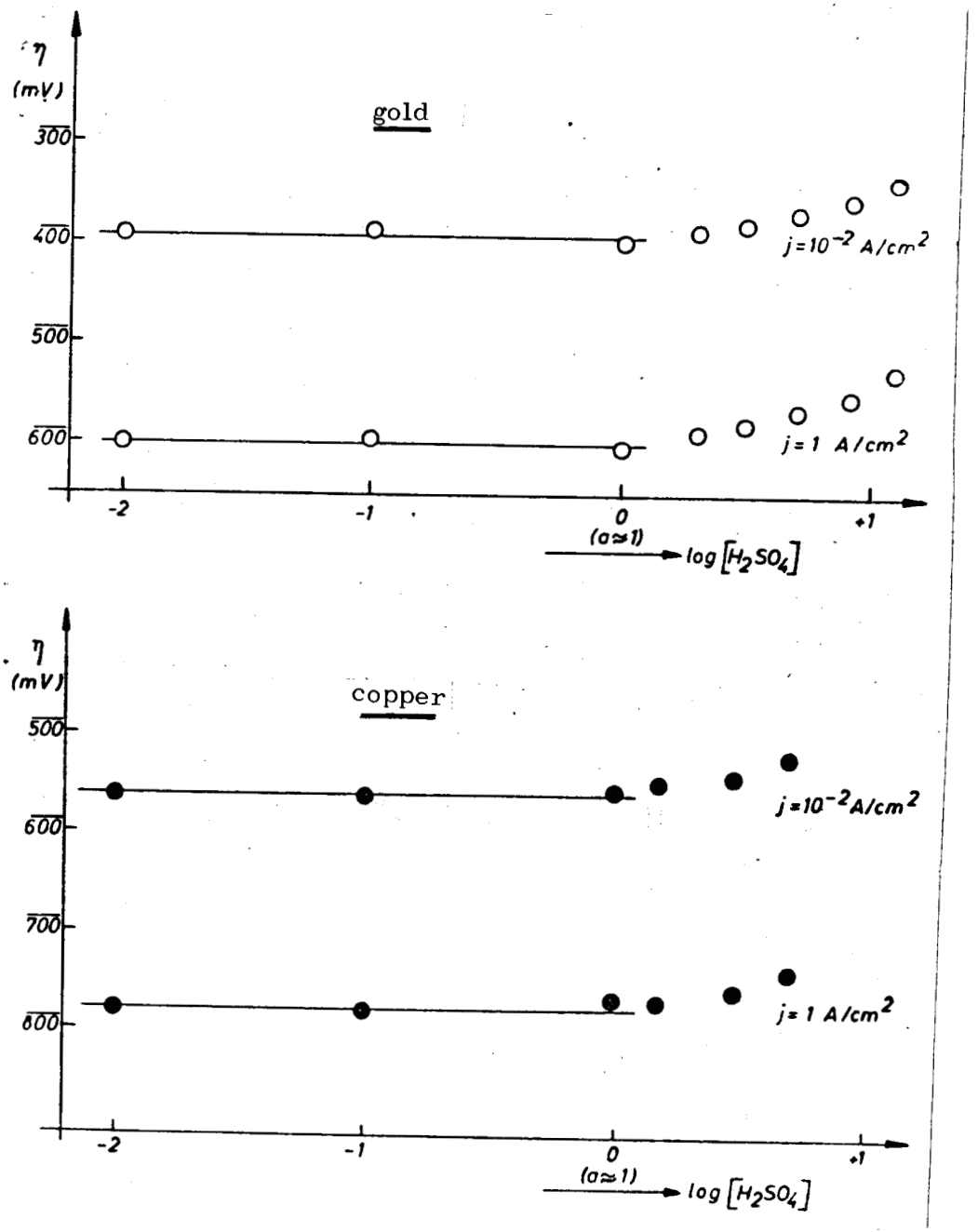


Fig. 5. pH-Dependence of Hydrogen Overtension on Copper and Gold in Pure Sulfuric Acid.

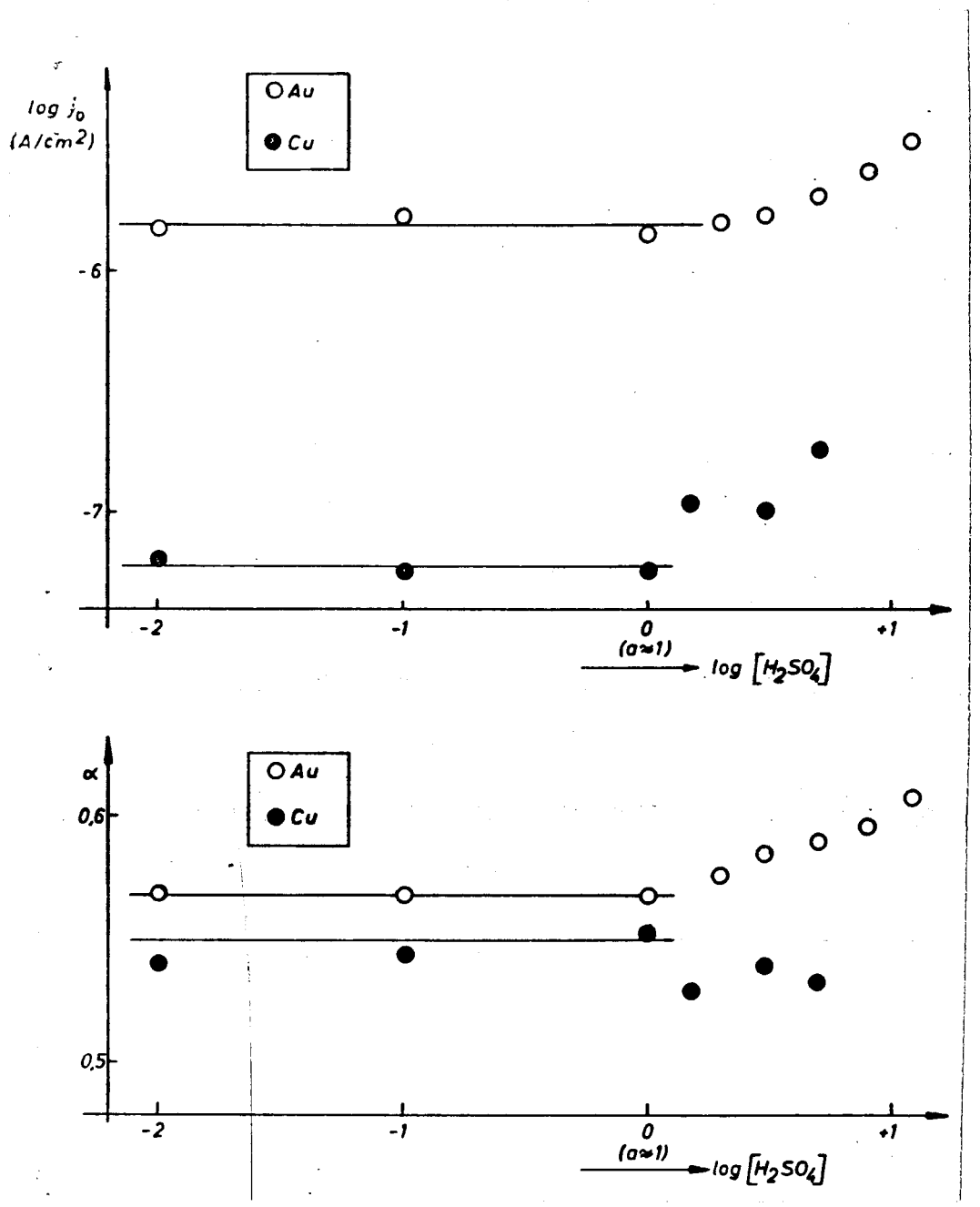


Fig. 6. pH-Dependence of the Effective Exchange Flux Densities (j_0) and Throughput Factors (α) of Cathodic Hydrogen Dissociation on Copper and Gold.

in the presence of specifically adsorbent ions), because the structure of the diffuse double layer appears to be determined by the electrolyte to a considerable extent. This is not the case, however, as we can see, e.g., from a comparison with other systems which have been investigated previously in this regard (Table IV).

The material from the references listed in Table IV generally /36
indicates a regular relationship between the overtension process and the ζ-potential of the electrodes, such that the ζ-limits are displaced toward smaller hydrogen ion concentrations with increasing activity of the electrode metals with respect to the hydrogen reaction (Pb, Hg < Ag, Cu, Au < Ni). An analysis of the conditions under which the overtension measurement ranges and possibly the Lippmann potentials of the charge-free electrodes can play a significant role will not be attempted here.

(4) The overtensions for copper and gold, up to the highest acid concentrations investigated here, show a normal curve according to the Frumkin formula. This finding is interesting in the light of the results obtained by Bockris and Conway [65] for Ag/HCl, according to which the overtension in 0.01n HCl (according to the theory) begins to become more positive, but then reaches an extreme in 1n HCl and finally becomes negative once again. The differences appear especially remarkable because this involves the behavior on the analogous metals silver and copper as well as gold. The authors [65] attempt to interpret their data in terms of a specific adsorption of hydrogen ions at high acid concentrations. According to our findings, such an absorption could occur only in special cases; perhaps a specific effect of the chloride anion should be discussed first [11].

(5) For the pH-dependence of the effective exchange flux density, with $\bar{\bar{\varepsilon}} = \bar{\bar{\varepsilon}}^{0} + (RT/F) \ln a$ ($\bar{\bar{\varepsilon}}^{0}$ = absolute normal potential), we obtain the following in logarithmic form:

$$\ln j_0 = \ln 2F\left[k' \exp\left(-\frac{\alpha F}{RT}\bar{\bar{\varepsilon}}^{0}\right)\right] + (1-\alpha)\ln a - \frac{(1-\alpha)F}{RT}\zeta$$

and therefore /37

$$\frac{\partial \ln j_0}{\partial \ln a} = \text{const.}\left(\frac{\partial \alpha}{\partial \ln a}\right)\begin{cases} +0 & \text{for } \zeta = \text{const} + \frac{RT}{F}\ln a \\ +(1-\alpha) & \text{for } \zeta = 0 \end{cases}$$

---

[11] The findings of Bockris and Conway are based on relatively inexact measured values. It is planned to make a new study of the relationships for silver, both with hydrochloric acid and sulfuric acid, using our precise measurement method.

Hence, the exchange flux density in the range $\zeta \neq 0$ is also independent of the concentration if the same is true for the throughput factor α. The condition

$$\frac{\partial \alpha}{\partial \ln a} = 0$$

is also a prerequisite for the validity of the Frunkim overtension formula.

From Table IV and Figure 6, we can obtain an experimental confirmation of such a constancy of log j_0 and α[12].

3b. Sign of the ζ-Potential

Salt-effect studies provide us with information on the sign of the ζ-potential. Addition of (nonspecifically adsorbed) neutral salts to the electrolyte cause a drop in the ζ-potential and consequently a reduction in the value of the corresponding term in the rate equations. If $\zeta > 0$ in the pure acid, the overtension becomes more positive; if $\zeta < 0$, it becomes more negative.

Figure 7 describes qualitative experiments on gold cathodes with the addition of various sulfates. We see that at the lower end of the measurement range, all of the salts had effects which were quantitatively the same, so that a specific cation influence can be excluded here. The effects which appear at higher overtensions and are evidently produced by incipient cation reactions are of no interest to the present problem.

We see from the displacement of the overtension curves that the ζ-potential is negative. Moreover, we can conclude from this that in the highly cathodic polarization ranges of our measurements, the absolute potentials ε are always more negative than the Lippmann potentials of the charge-free electrodes.

Experiments with cathodes made of copper and alloys (Cu-Ga III, Au-In II) yielded similar results.

3c. ζ-Potential and Throughput Factor [44] /38

The ζ-potential is also a function of the electrode polarization. For values of ζ that are not too high, there is an approximately linear relationship:

$$\zeta = \bar{\bar{\zeta}} + \left(\frac{C_{DS}}{C_d}\right)\eta ;$$

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[12] The log j_0-values are scattered to a somewhat greater degree, because the errors in a_T and b enter into their calculation (log $j_0 \sim a_T/b$).

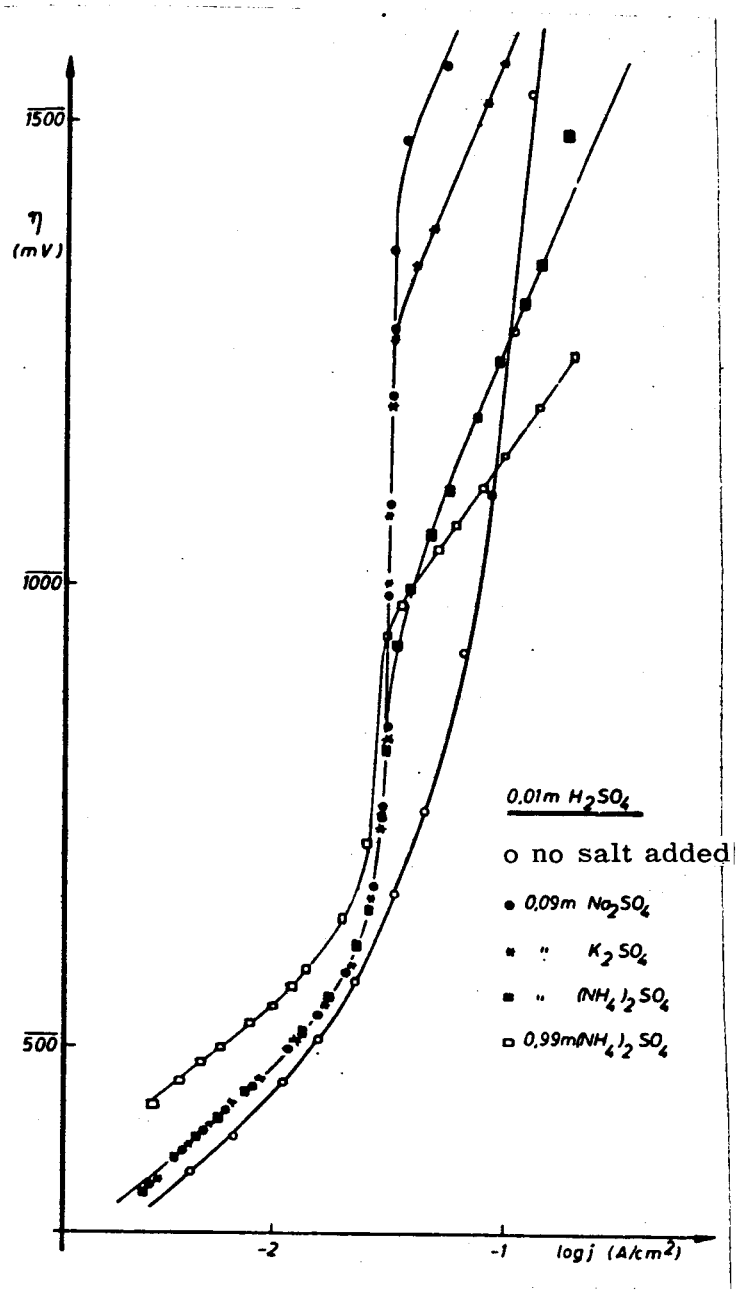

Fig. 7. Change in Overtension With Addition of Conducting Salt. Gold Cathodes, T = 20° C.

C_{DS} and C_d are the capacities of the entire and diffuse double layers, respectively. The linear term appears only in the overtension term of the current-potential equation, so that it only produces a modification of the Tafel slope b and the throughput factor α. For this experimentally determined, so-called "effective" throughput factor α^*, we have:

$$\alpha^* = \alpha + (1-\alpha)\frac{C_{DS}}{C_d} .$$

The value α^* is therefore somewhat larger than the actual throughput factor; according to Vetter [44], the difference is about 5-10%. The empirical α^*-values in the present investigations lie predominantly between 0.52 and 0.58, so that we obtain amounts for the actual throughput factors which differ only slightly from the value of $\alpha = 0.50$ used in the theory[13].

These concepts are based on the relationships with $\zeta \neq 0$. The increase of the throughput factor at high acid concentrations (where $\zeta = 0$)[14] are not related to the ζ-potential but must be caused by changes in the double layer structure.

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[13] In the following, we will forego a correction and special description of the effective throughput factor.

[14] Similar results were obtained by Yofa and Frumkin for 3n-12.5n HCl [49,51].

CHAPTER V

OVERTENSION AND CONTACT SPECIFICITY

The properties of the electrode material are revealed (in a given mechanism) by the special position of the current-potential curves. Their experimental characteristic value is the exchange flux density. As far as purely kinetic problems are concerned, their value as such is of no importance; studies of the specificity problem, on the other hand, must be based on its theoretical expression, whose formulation will now be discussed in detail.

The designation of the specific relationships in an electrode system is performed in the usual case on the basis of individual values of the exchange flux densities obtained usually for room temperature. A single exchange flux density, however, gives information only with respect to the gross reactivity, which is simultaneously dependent upon several specificity parameters. A thorough treatment of the problem of specificity requires a careful analysis of the various influences and presupposes a knowledge of the thermal behavior of the reaction.

The relationships are formulated according to the theory of absolute reaction rates. We shall express them in terms of the examples of mechanisms of interest in this paper. For the sake of simplicity, we will assume $\zeta = 0$.

1. THEORETICAL EXCHANGE FLUX DENSITIES

According to the theory of Eyring [66], the absolute rate of an elementary reaction is:

$$v = \kappa \frac{kT}{h} \exp\left(-\frac{\Delta G^{\ddagger}}{RT}\right) \pi (c_r)$$

$$= \kappa \frac{kT}{h} \exp\left(\frac{\Delta S^{\ddagger}}{R}\right) \exp\left(-\frac{\Delta H^{\ddagger}}{RT}\right) \pi (c_r)$$

κ = Transition coefficient[15]

[15] In the present case, κ can be equated to 1 and omitted.

k = Boltzmann's constant
h = Planck's constant
$\Delta S^{\pm}$ = Activation entropy
$\Delta H^{\pm}$ = Activation enthalpy
$\Pi(c_T)$ = Product function of reactant concentrations (reaction order).

For the Volmer step, we have /40

$$(\Pi(c_r))_V = N_{\textcircled{M}}\, a,$$

for the Horiuti step

$$(\Pi(c_r))_H = N_{H\,\textcircled{M}}\, a.$$

In the above, the number of free reaction centers of the cathode surface and the number of reaction centers occupied by chemisorbed hydrogen atoms (a = hydrogen ion activity) are represented by $N_{\textcircled{M}}$ and $N_{H\,\textcircled{M}}$, respectively. On the basis of the total number N_M of interaction centers of the cathode metal which are lost per unit area,

$$N_{\textcircled{M}} = N_M(1-\vartheta),$$

$$N_{H\,\textcircled{M}} = N_M\vartheta.$$

The corresponding rate equations can therefore be written in the following form:

$$V_V(\varepsilon) = \frac{kT}{h} N_M \exp\left(\frac{\Delta S_V^{\ddagger}}{R}\right) \exp\left(-\frac{\Delta H_{V,M}^{\ddagger}(\varepsilon)}{RT}\right)(1-\vartheta)\, a$$

$$V_H(\varepsilon) = \frac{kT}{h} N_M \exp\left(\frac{\Delta S_H^{\ddagger}}{R}\right) \exp\left(-\frac{\Delta H_{H,M}^{\ddagger}(\varepsilon)}{RT}\right)\vartheta\, a$$

By using the explicit expressions for the $H^{\pm}(\varepsilon)$, we obtain the following formulas for the exchange flux densities of the total reaction:

$$j_0 = \frac{2FkT}{h} N_M \exp\left(\frac{\Delta S_V^{\ddagger}}{R}\right) \exp\left(-\alpha_{V,M}\frac{F}{RT}\bar{\bar{\varepsilon}}_M\right) \exp\left(-\frac{\Delta H_{V,M}^{\ddagger}}{RT}\right) a$$

$$j_0 = \frac{2FkT}{h} N_M \exp\left(\frac{\Delta S_H^{\ddagger}}{R}\right) \exp\left(-\alpha_{H,M}\frac{F}{RT}\bar{\bar{\varepsilon}}_M\right) \exp\left(-\frac{\Delta H_{H,M}^{\ddagger}}{RT}\right) a,$$

depending on whether the Volmer step or the Horiuti step (Case IIa) determines the kinetics ($\Delta H_M^{\pm}$ = activation enthalpies at $\varepsilon = 0$). The individual characteristics of the electrode material enter into /41 the exchange flux densities with N_M, $\Delta H_M^{\pm}$, and $\bar{\bar{\varepsilon}}_M$; in addition, the throughput factors also appear to be somewhat dependent upon

the material, and for this reason we have provided them with the material subscript M in the above formulas.

To the extent that there have been any attempts made at all in the literature to provide explicit formulations in the above sense or to make corresponding statements regarding the material-dependence of the kinetic parameters, there is always a failure to consider the concentration of centers N_M (see also [53, 54, 67, 68]). The relative values of ϑ and $1-\vartheta$ of the degree of coverage have been used falsely to indicate the numbers of centers, with no attention being given to the fact that those values should really be written as $N_M\vartheta$ and $N_M(1-\vartheta)$. The shortcomings involved in the consideration of the $\bar{\bar{\varepsilon}}_M$ potential have already come to light in Chapter IV, Section 2.

The specific number of centers N_M is determined by geometric contact parameters, while the values of $\Delta H_M^{\pm}$ and $\bar{\bar{\varepsilon}}_M$ are determined by energy (electronic) contact parameters. Since the latter are not directly related to one another, but act as independent factors, individual values for exchange flux densities or overtensions cannot provide any unambiguous contact-chemical specifications for an electrode system. Two examples should suffice to illustrate and prove the existence of this state of affairs.

In our studies of the overtension behavior of alloys[16] we initially limited ourselves to the method of direct comparison of characteristic overtensions or exchange flux densities, which had previously been convenient. While in the case of the initially investigated silver alloys [69] definite regularities were found, the analogous gold alloys [70b] at room temperature showed a nearly exact independence of the overtension values from the cathode material, while the copper alloys showed a completely unsystematic behavior (Fig. 20). These findings contradict one another and do not correspond to the contact behavior which one would expect for these materials on the basis of theoretical and catalytic investigations. An attempt to explain it by using a theory of Parsons [68], where the exchange flux densities can remain constant for certain ranges of heat of adsorption of the hydrogen bonded to the /42
electrodes (H Ⓜ), was also unsuccessful. These discrepancies led the author to conduct a thorough test of the method previously used and the formulations which form the basis of it. We shall see that the irregularities can be explained by compensation effects between the various contact influences.

2. FREQUENCY FACTORS AND ACTIVATION ENERGIES

The exchange flux densities for unit concentrations of reactants are expressed in electrical units and rate constants extrap-

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[16] For further details, see Chapter VIII.

olated to $\eta = 0$. As such, they constitute products of the frequency factors (J_0) and the exponential functions of the activation energies:

$$(j_{oM})_{\pi(c_r)=1} = J_{oM} \exp\left(- \frac{\Delta H^{\ddagger}(\bar{\bar{\varepsilon}}_M)_M}{RT} \right)$$

For purposes of convenience, the number of centers N_M per unit surface has been chosen as the unit of center concentration; this means that it enters into the frequency factor as a characteristic contact parameter. In this way, a complete contact-chemical characterization of a system is obtained in terms of the frequency factor and the activation energy.

In the event that the electrode reaction follows an Arrhenius relationship, the values of the frequency factors and the exponential terms can be determined individually from its thermal behavior, and the geometric and energy reaction parameters of the exchange flux densities can be obtained separately later.

2a. Frequency Factors

For the two mechanisms considered in Section 1, we have the following expressions for the (electrochemical) frequency factors:

$$J_{oM} = \frac{2FkT}{h} N_M \exp\left(\frac{\Delta S_V^{\ddagger}}{R} \right)$$

$$J_{oM} = \frac{2FkT}{h} N_M \exp\left(\frac{\Delta S_H^{\ddagger}}{R} \right)$$

The activation entropies $\Delta S_V^{\pm}$ and $\Delta S_H^{\pm}$ are determined by the nature of the mechanism alone. Hence, they have nearly the same value for all electrode systems with the same electrolyte and reaction conditions. This means that the specific numbers of centers N_M are generally critical for the individual frequency factors; they can be considered only after a discussion of the differences which appear. /43

2b. Activation Energies

The exchange flux densities are not based on the electrochemically identical state of the absolute zero potential ($\varepsilon = 0$), but on the electrode-specific equilibrium potentials ($\varepsilon = \bar{\bar{\varepsilon}}_M$) which can be determined exactly by experiment. This means that we must differentiate between the critical "equilibrium-activation energy" which is related to the exchange flux density

$$\Delta H_M^{\ddagger}(\bar{\bar{\varepsilon}}_M) = \Delta H_M^{\ddagger} + \alpha F \bar{\bar{\varepsilon}}_M = \Delta H_M^{\ddagger} + \alpha F C_E - \frac{\alpha F}{e_o} \Phi_M$$

(cf. p. 30)

and the activation energy, reduced to the corresponding states, is:

$$\Delta H_M^{\ddagger}$$

$$(\text{and } \Delta H_M^{\ddagger} + \alpha FC_E)$$

The specific interaction energy relationship between the substrate and the contact is characterized by the activation enthalpy $\Delta H_M^{\pm}$. However, the exchange flux densities contain the equilibrium-activation enthalpies $\Delta H^{\pm}(\bar{\varepsilon})_M$ as exponents. Therefore, any precise statements regarding the interaction energy situation presuppose a knowledge of the absolute potentials or work functions, or at least some definite ideas regarding their values or their functional relationship to $\Delta H_M^{\pm}$.

The dependence of the activation energy upon the material is primarily the result of a similar relationship for the heat of adsorption of atomic hydrogen[17]; this is because the latter determines the relative positions of the reactant and product curves in the reaction energy diagrams for the elementary processes (see Fig. 29) [73]. On the other hand, this means that overtension studies can provide significant information regarding the adsorption properties and especially the contact-chemical behavior of the materials used as electrodes. /44

If the Tafel step, the combination of two adjacent adsorbed hydrogen atoms, determines the mechanism, the reaction energy picture can also depend on stereochemical factors (dependence on the interval between the chemisorbed reactants). In the other cases discussed here, stereochemical problems play a subsidiary role, so that it is primarily electronic and chemical factors that are involved in the latter.

3. TEMPERATURE-DEPENDENCE OF EXCHANGE FLUX DENSITIES

The temperature interval which can be comfortably investigated by experimentation covers about 60°. Within a range of this order, the center and reactant concentrations can be treated as constants. The temperature dependence of the energy values $\Delta G^{\pm}$ (as well as $\Delta H^{\pm}$ and $\Delta S^{\pm}$) and , on the other hand, is of basic significance. Our studies also showed that in many cases the throughput factors can also change with temperature.

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[17] A relationship between the overtension and adsorption processes was mentioned previously by K. F. Bonhoeffer [71]; J. Horiuti and M. Polanyi [72] were the first to discuss the relationships (for the Volmer step) in explicit form.

We obtain the following as a general Arrhenius function of the exchange flux densities:

$$-R\left(\frac{\partial \ln j_{oM}}{\partial\, 1/T}\right) = RT + \Delta H_M^{\ddagger} + \alpha_M F\bar{\bar{\varepsilon}}_M - \alpha_M FT\left(\frac{\partial \bar{\bar{\varepsilon}}_M}{\partial T}\right) - FT\bar{\bar{\varepsilon}}_M\left(\frac{\partial \alpha_M}{\partial T}\right) .$$

(The respective values here must still be provided with the subscript for the reaction-determining step.) The last term drops out for constant α. The temperature functions of $\Delta S^{\pm}$ and $\Delta S^{\pm}$, according to the thermodynamic fundamental relationships, assume the following form:

$$\left(\frac{\partial \Delta S^{\ddagger}}{\partial T} = \frac{1}{T}\frac{\partial \Delta H^{\ddagger}}{\partial T}\right).$$

Since $F\bar{\bar{\varepsilon}}_M = \Delta G_M$, we also have: /45

$$\alpha_M FT\left(\frac{\partial \bar{\bar{\varepsilon}}_M}{\partial T}\right) = -\alpha_M (T\Delta S_M)$$

and (Gibbs-Helmholtz equation):

$$\alpha_M F\left(\bar{\bar{\varepsilon}}_M - T\left(\frac{\partial \bar{\bar{\varepsilon}}_M}{\partial T}\right)\right) = \alpha_M \Delta H_M ;$$

where ΔG_M, ΔH_M and ΔS_M are the caloric reaction values of the electrode process:

$$\frac{1}{2}H_2 \longrightarrow H^+_{aq} + e^-(M)$$

when electrode metal M is used.

3a. Experimental Activation Energies

All of the reaction systems treated in the present paper offer Arrhenius relationships between ln j_0 and 1/T which are linear within the limits of error. The changes

$$\alpha F\int_{\Delta T} T\frac{\partial \bar{\bar{\varepsilon}}}{\partial T}\,dT + F\bar{\bar{\varepsilon}}\int_{\Delta T} T\frac{\partial \alpha}{\partial T}\,dT$$

in the Arrhenius function within the measured temperature inter-

val ΔT are negligibly small in these cases; for the experimental activation energies q_M, obtained from the measurement diagrams, we have

$$q_M = -R\left(\frac{\partial \ln j_{oM}}{\partial\, 1/T}\right) .$$

The experimental activation energies differ from the contact-chemically significant $\Delta H^{\ddagger}$ in those terms which are also dependent upon the electrode material. This dependence is produced not only by the equilibrium potentials $\bar{\bar{\varepsilon}}_M$, but generally by the throughput factors as well.

With different α-values, there is a definite uncertainty even for the relative activation enthalpies in comparison investigations, even if the differences between the individual equilibrium potentials (exit and contact potentials) are known exactly. For the relative values of the actual and experimental activation energies of two reaction systems with cathode metals M_1 and M_2, we obtain a simple calculation as a general relationship: /46

$$\Delta H^{\ddagger}_{M_2} - \Delta H^{\ddagger}_{M_1} = q_{M_2} - q_{M_1} + \left[\left(\frac{\partial \alpha_{M_2}}{\partial T} - \frac{\partial \alpha_{M_1}}{\partial T}\right) T - \Delta\alpha_{M_2M_1}\right] F\bar{\bar{\varepsilon}}_{M_1} + \left[\left(\frac{\partial \alpha_{M_2}}{\partial T}\right)_T - \alpha_{M_2}\right] F K_{M_2M_1}$$

with $\bar{\bar{\varepsilon}}_2 = \bar{\bar{\varepsilon}}_1 + K_{21}$ and $\alpha_2 = \alpha_1 + \Delta\alpha_{21}$. The negligible terms with $(\partial\bar{\bar{\varepsilon}}/\partial T)$ have been omitted.

3b. Experimental Frequency Factors

The real frequency factors (J_{0M}) are related to the experimental values (A_M) obtained from the empirical Arrhenius curves

$$\ln j_{oM} = \ln A_M - \frac{q_M}{RT} \qquad (+ \ln a)$$

by the equation

$$\ln J_{oM} = \ln A_M - \ln e + \frac{F}{R}\left(\frac{\partial \alpha_M \bar{\bar{\varepsilon}}_M}{\partial T}\right)$$

(e = base of the natural logorithm). An estimate will show that the last term can be disregarded for all possible as well as en-

countered values of ε, α, $\frac{\partial \varepsilon}{\partial T}$, $\frac{\partial \alpha}{\partial T}$ [18]; hence, the real frequency factors can be determined practically exactly within the limits of accuracy of the A_M-values.

[18] The errors introduced by this omission are still smaller when the relative values are compared.

CHAPTER VI

REPRODUCIBLE OVERTENSION MEASUREMENT

In the preceding chapters, we have familarized ourselves with /47
the basic theoretical problems involved in contact-chemical overtension investigations and (where necessary) we have pointed out shortcomings and errors in principle contained in previous analyses while formulating correct relationships. In addition to these theoretical shortcomings, an unimpeded treatment of overtension problems has been hindered thus far by a fundamental experimental difficulty: the measurements were very poorly reproducible.

Faulty reproducibility, which could be improved only with considerable difficulty, is a feature of all contact reactions and has played a significant role in studies of overtension. The reason for this is the two-dimensional character of this reaction system (cf. Chapter I) which means that on the one hand, extremely small amounts of impurities can suffice to change the reaction zones completely and on the other hand, that an adequate explanation of the states of such interfacial regions is made difficult or completely impossible. This often makes a definite preparation impossible.

The problem of the reproducibility of electrode processes has already been discussed many times; Bockris dealt with it in detail with respect to the hydrogen dissociation reaction and described a method for obtaining better results [43]. Bockris assigned special significance to the purity of the electrolytes and therefore insisted on the maintenance of vigorous experimental conditions. Bockris' method is complex and time consuming and requires considerable expenditure for apparatus. For example, the substrate must be multiply distilled and introduced into the reaction cell under hydrogen; the electrolyte must then be pre-electrolyzed in the cell for several days prior to each experiment; in addition, the electrodes must be tempered in hydrogen and sealed into protective ampoules under hydrogen.

In our experiments, we initially observed these requirements to a considerable degree. Despite painstaking care, we met with only moderate success in reducing the degree of scatter of the measured values to the point where any evaluation could be made at all

(see [69] and the results of the "standard" experiment in [70a and b]). Further purification of the substrate failed to show any improvement, and we also determined by means of electron diffraction that even the fresh surfaces of carefully prepared cathodes, tempered in pure hydrogen, could contain layers of impurities. These findings indicated that as far as reproducibility was concerned, /48
it was mainly a question of the state of the fresh cathode surfaces.

In further investigations, however, the author has now succeeded in developing a method which ensures a complete reproducibility of the experiment [74]. This "abrasion method", in which the electrode surfaces are kept in a fresh condition by abrasion, is also distinguished by a simple and rational experimental procedure.

The measurements discussed in the present paper are based primarily on abrasion tests.

1. Abrasion Method

The first abrasion measurements were conducted in a special connection as preliminary tests under conditions as simple as possible: an open vessel served as an electrolysis cell; the electrolyte (analytically pure sulfuric acid) was not refined further; the abrasion was performed manually, using a glass rod cut to a sharp angle. Even these simple experiments had as their unexpected result extremely reproducible measurements (see Fig. 8).

Perfection of the method required only a mechanization of the abrasion process for a simplified and more definite experimental procedure. Recently, a sealed abrasion cell has been constructed for measurements in the absence of air or under special gas atmospheres.

In the abrasion experiments, a mechanically driven ruby scraper travels over the electrode surface at a given frequency (usually about 10 Hz); the frequency is selected so that a complete formation of the stationary double layer is ensured following each pass of the scraper. The test electrodes are in the form of wires inside plexiglas housings filled with araldite; to prepare the reaction surfaces, they are cut diagonally.

1a. Reproducibility and Incorrect Measurements

The efficiency of the abrasion method was evaluated in all /49
investigations, which resulted in a very large number of measurements on different cathodes. In summary, it was found that:

(1) In contrast to the earlier measurement methods, incorrect measurements are encountered only occasionally in the abrasion method; even these lie within narrow limits of scattering and can therefore be disregarded as a rule [19].

19 This is usually due to improper abrasion. The quality of the abrasion is tested after each experiment by a microscopic examination of the surface.

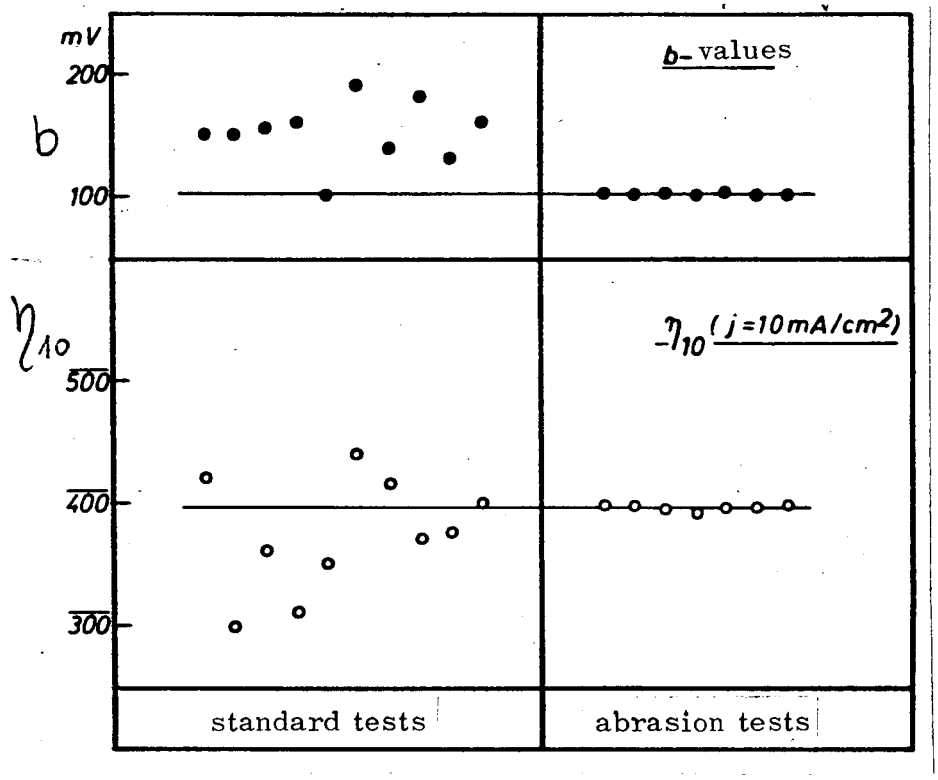

Fig. 8. Representative Measurement Results From Abrasion Tests and Tests With Unscraped Electrodes in Highly Purified Electrolytes ("Standard Tests"). Tafel Slopes (b) and η_{10}-Values for Gold Cathodes in 2n-Sulfuric Acid at Room Temperature.

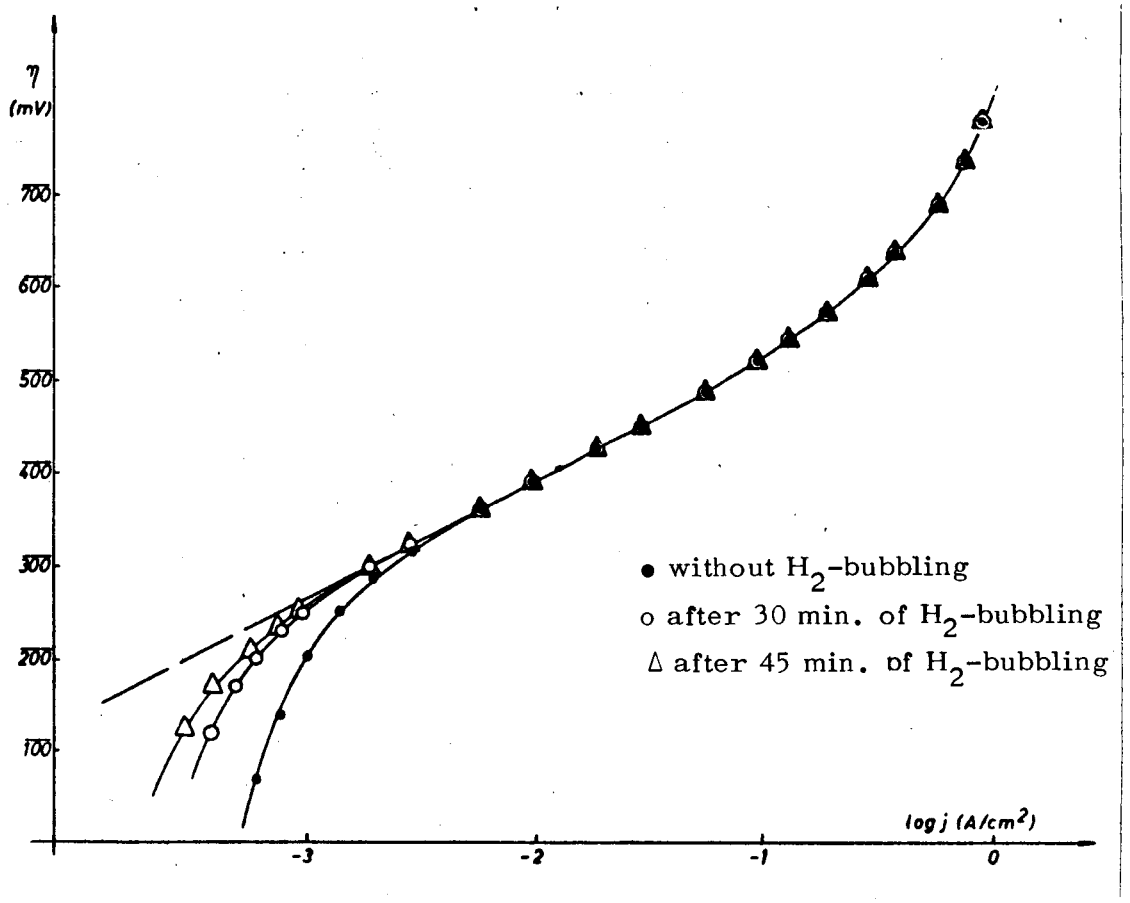

Fig. 9. Influence of Hydrogen Bubbling on Overtension Measurements in an Open Electrolysis Cell.

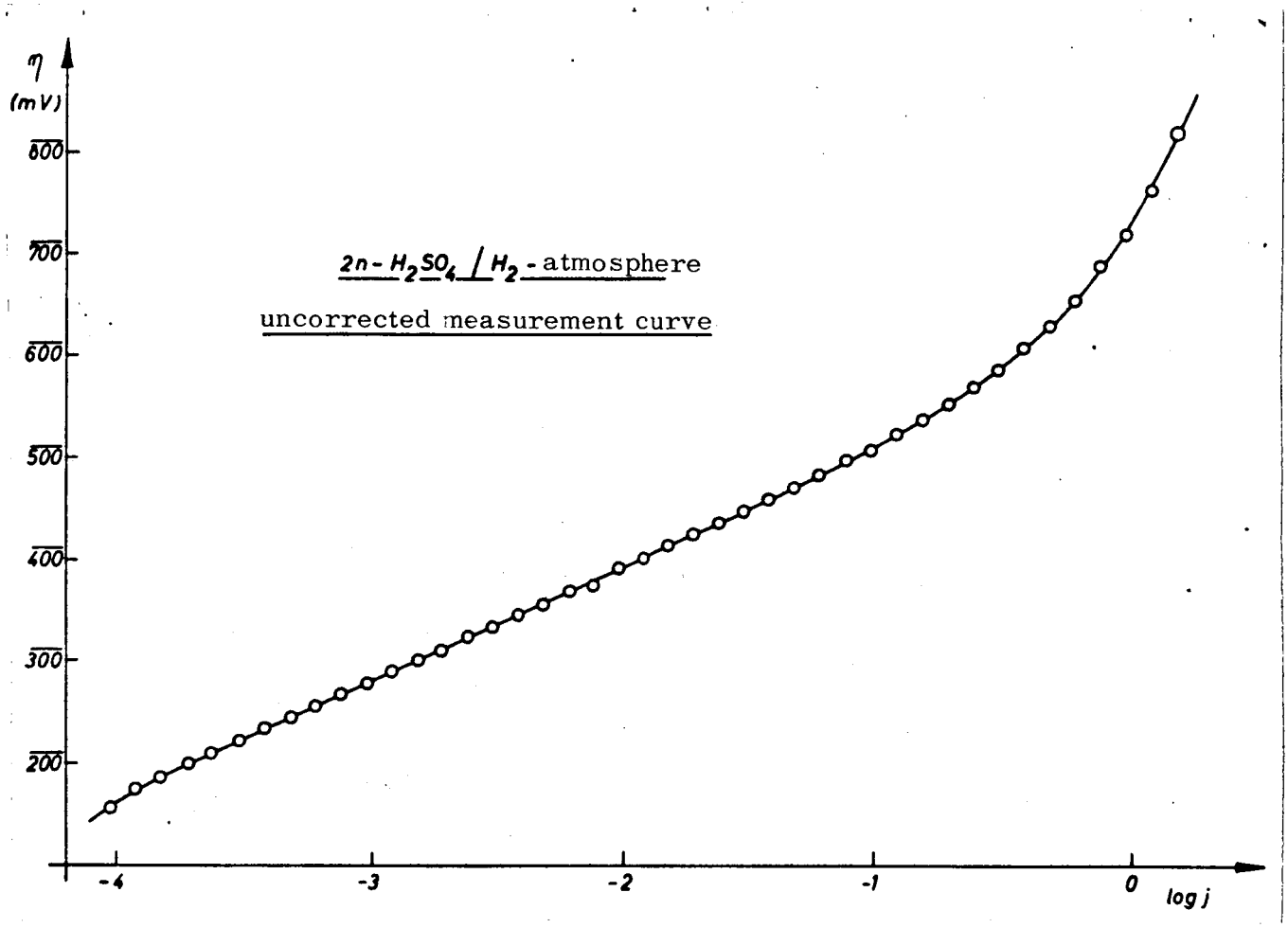

Fig. 10. Current-Potential Curve for a Gold Cathode With Exclusion of Oxygen.

(2) The reproducibility is determined by the pure measurement accuracy of the experimental system.

(3) The scatters of the measured overtension were found to be equal to $\Delta\eta < \pm 3$ mV. The parameters of the Tafel curves obtained have the following general scatters:

$$\Delta a_T \approx \pm 3 \text{ mV}$$
$$\Delta b \approx \pm 1 \text{ mV}$$
$$\Delta \log j_0 \approx \pm 0,05$$

Good results for abrasion measurements can be obtained even with limited apparatus and expenditure of time. Extreme cleaning of the substrate is unnecessary, as is a prolonged pre-electrolysis. The preparation of the electrode surfaces is considerably simplified; the constant renewal of the surfaces is of particular importance in the study of electrodes that can be attacked, especially those made of alloys. The abrasion also has a favorable effect on the bubble formation of the dissociated hydrogen, which is known to cause highly disturbing variations in the measured values at higher flux densities.

The performance of the tests in open vessels also yields reliable results as long as measurements in flux density ranges above the influence limit of oxygen are involved; according to Hickling and Salt [75], the depolarizing effect of oxygen is negligible above $j \approx 10^{-4} - 10^{-3}$ A/cm^2. Figure 9 shows the significance of bubbling hydrogen through the electrolyte during experimentation in an open electrolysis cell. Figure 10 shows the current-potential curve for a measurement conducted under a pure hydrogen atmosphere in a field cell; it shows how reliable results can be obtained by abra- /50
sion measurements without special electrolyte purification even in small overtension-current ranges. The diagrams also serve as further proofs of the efficiency of the method.

2. Measured Values in Abrasion Tests

The relationships in abrasion tests have already been studied in detail in another respect [74, 76, 77]. In the abrasion method, a distinction must be made between the resting value and effective value measurements, depending on whether the measurement is conducted after interrupttion of the abrasion or while it is still going on. It has been found that as a rule both types of measurements are suitable for obtaining correct overtension relationships. Under certain conditions, the differences which appear present interesting possibilities for a study of the boundary layer conditions.

2a. Abrasion Process

In one complete period, the scraper passes over the cathode surface twice, removing material; this means that the electrochemical boundary layer is destroyed briefly in the abraded areas. In between these times, the scraper moves above or below the cathode surface for a period of time; during these intervals, the boundary layer regenerates completely to reach the stationary state. The regeneration time is short relative to the duration of an abrasion period; for the systems investigated, it generally lies between 10 and 30 msec. Fundamentally speaking, the abrasion frequency is a new experimental parameter, whose optimum value changes markedly only with extreme changes in the electrode process.

The abrasion process was tested oscillographically for a number of electrode systems. A representative result is shown in Figure 11.

The oscillograms were made with a two-beam oscillograph (Tektronix Type 502). The upper beam was used to show the hydrogen overtension, and the lower was used to show the strength of the electrolysis current (voltage drop across a fixed resistance). The circuit was not strictly galvanostatic, so that the tendency of the current behavior was visible in the experiments.

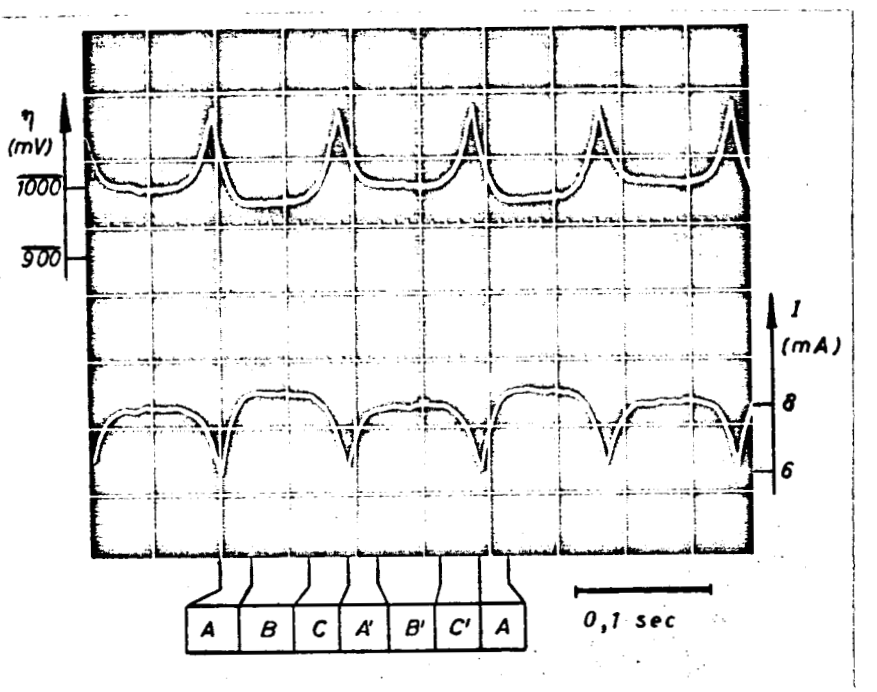

Fig. 11. Abrasion Process at High Flux Density ($j \approx 1.5$ A/cm^2). Alloy Cathode (Cu-Ga III) in 2n-H_2SO_4 at 20° C. A, A': Regeneration of the Double Layer; B, B': Stationary State; C, C': Removal of Surface Layer. During A, B the Scraper is Above the Electrode Surface; During A', B' it is Below the Electrode Surface.

The abrasion causes a temporary reduction of the effective cathode surface and hence reduces the effective double layer capacity. This results in a rise in the overtension (with a simultaneous drop in the current). The pattern of the intermediate periods show the complete regeneration of the stationary state [20]. /51

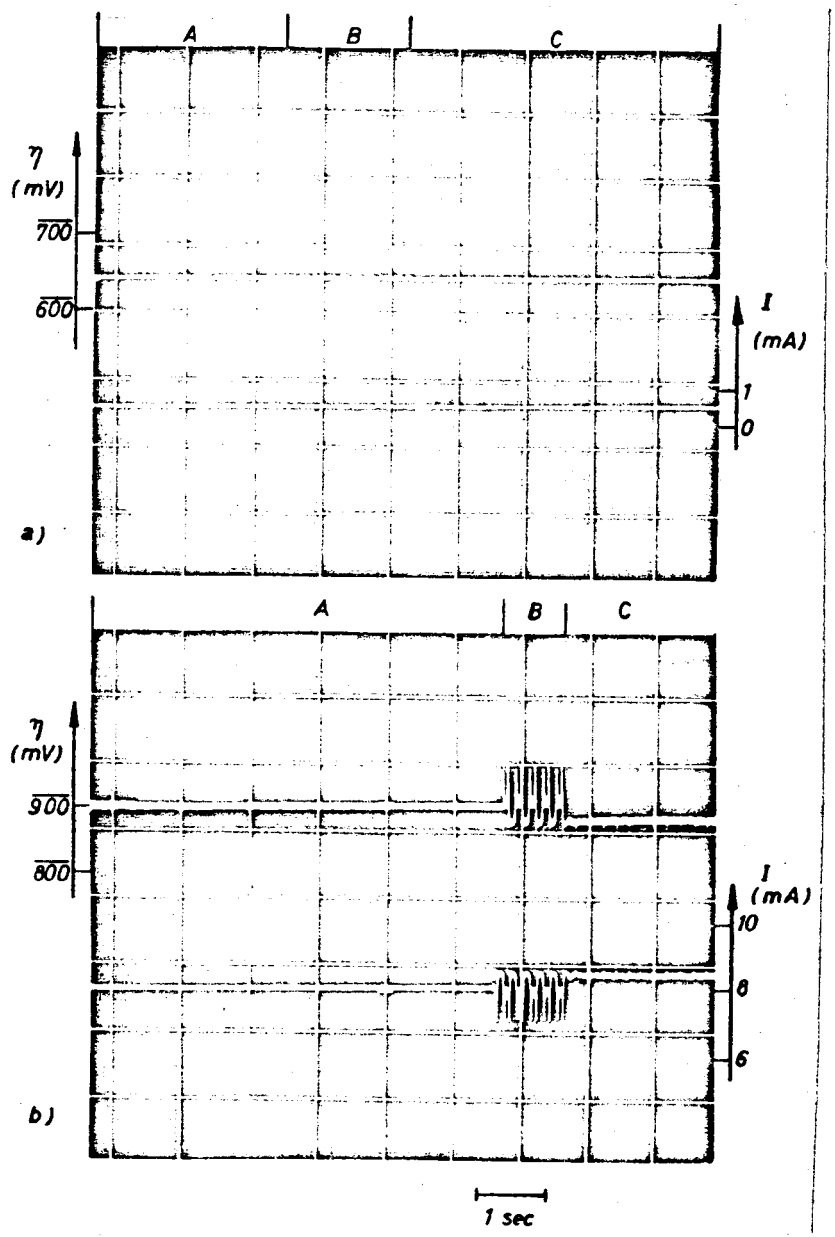

Fig. 12. Effective Values (A), Fluctuation Values (B) and Resting Values (C) in the Abrasion Process. Copper Electrode in 2n-H_2SO_4 at T = 20° C. (a) Flux Density $j \approx 0.07$ A/cm^2; (b) Flux Density $j \approx 1$ A/cm^2. Equal Ordinate Scales.

[20] The differences in the half-periods of the abrasion process are caused merely by the special position of the scraper and can be avoided by shifting the latter; they have no significance for the reaction conditions or the evaluation. For details in this regard, see [75].

2b. Effective Values, Fluctuation Values, Resting Values

Figure 12 shows the relationships between these values for a (high) flux density, in which the effective values differ sharply from the resting values, as well as for a (smaller) flux density, at which the differences are negligible.

The recording of the effective values is performed by inserting integrating circuits into the measurement circuit.

2c. Measured and Corrected Overtensions. Ohmic Overtension

In the abrasion tests, the lead to the reference electrode (Luggin lifter) is not connected directly to the test electrode; the measured overtensions therefore contain ohmic potential components. The ohmic overtensions are neglibibly small for electrolysis flux densities below a value of approximately 10^{-1} - 10^{-2} A/cm^2 (see Fig. 10, for example); they increase with increasing flux density and must be taken into account in the evaluation of tests in higher ranges.

The ohmic overtension components, as terms which are linearly dependent upon the current, can readily be eliminated by calculation or graphically [21].

Similar viewpoints are valid with respect to the differences between the effective and the resting values. All previous experiences with the measurement range which is usually investigated (flux densities of approximately 10^{-3} - 1 A/cm^2) and the effective value deviations also change practically linearly with the current and are therefore included in the ohmic corrections. This means that in order to obtain the correct results, it is also a good idea to perform measurements during the abrasion and to omit the more complicated resting-value measurements, if this is a case, which can be determined on the basis of individual test experiments.

Relationships are clarified in Figure 13. The upper curve (η_{eff}) shows an experimental current-potential curve composed of effective values, while the middle curve (η_{rest}) shows the corresponding resting value relationship. Both curves (after correction) produce the same Tafel line ($\eta_T = a_T - b \log j$). The following relationships are valid:

$$\eta_T = \eta_{rest} - C_{rest} \cdot j = \eta_{eff} - C_{eff} \cdot j$$

or, if we use the current intensities I:

---

[21] Methods of evaluation have been developed by Freyer, Mansfeld, and Hodum in their theses [78-80].

$$\eta_T = \eta_{rest} - R_{rest}I = \eta_{eff} - R_{eff}I, \qquad /52$$

where the "resistances" R and the "resistance factors" C = R × electrode surface F are experimental constants.

The correction terms for resting values are pure ohmic potential components, whose values can also be obtained by correction experiments (Fig. 14), for example.

The ohmic potential difference η_Ω = RI is located almost completely in the immediate vicinity of the electrode. This is shown by experiments in which the Luggin lifter was moved in the electrolysis cell without any measurable overtension changes occuring. Such conditions can generally be expected in cell systems for which the electrode surfaces are much less than the cross section of the cell.

3. Discussion of the Abrasion Method

Our comprehensive data show that the specific influence of the cathode material is not obscured by the abrasion. The agreement found in numerous and diverse cathode systems between the overtension values of abraded electrodes and the approximate or cumulative values for corresponding unabraded electrodes also show that as a rule the overtension characteristics of an electrode are not altered appreciably by abrasion [74] (see Fig. 8).

3a. Overtension Behavior and Real Structure

Since abrasion undoubtedly produces a certain modification of the surface structure of the electrode, which differs slightly from case to case, we can conclude on the basis of the situation as described above and the conditions for reproducibility in abrasion experiments, that the real structural parameters of a contact material (crystallinity, deformation, etc.; cf. Section II.3) probably have hardly any significant influence. In particular, the abrasion causes no activation of the contacts in this case [22].

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[22] In the case of hydrogen peroxide dissociation on silver, in which we first studied the application of the abrasion method to catalytic processes, the abrasion produces (among other things) a significant rise in the activity of the contact. The corresponding investigations show that definite real structure parameters must play a critical role in this reaction. The abrasion method is seen to be a valuable investigational criterion in this respect. See also [81].

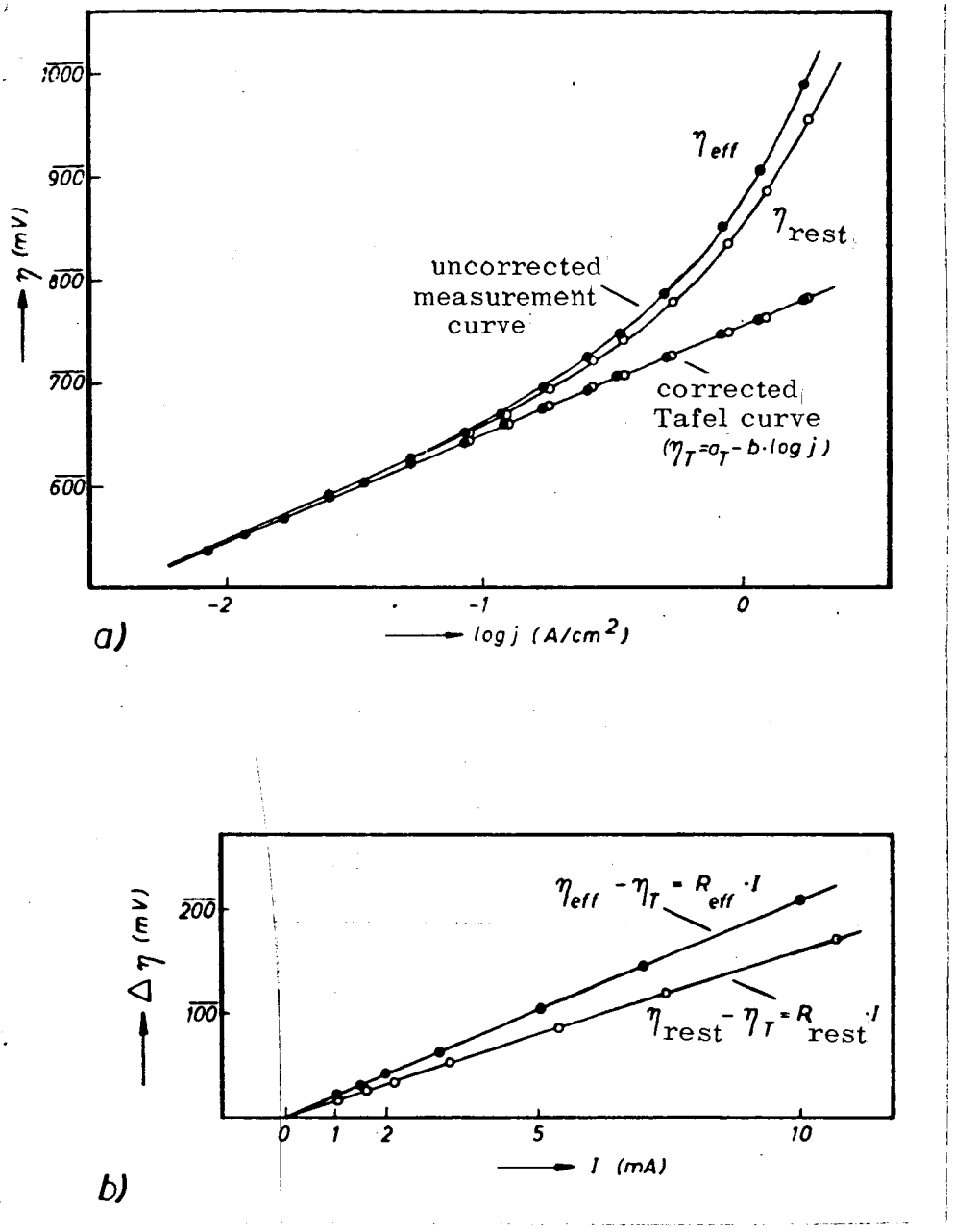

Fig. 13. Plot of a Tafel Curve (Cu in 2n-H_2SO_4 at 20° C. (a) Current-Potential Curves; (b) Correction Lines.

3b. Special Applications of the Abrasion Method

The basic agreement of the properties of abraded and unabraded electrodes can be tested in a study of new systems by individual test experiments. In the case of a disagreement, there is the possibility that the findings for the unabraded electrodes can be attributed to modifications of the cathode material by gas adsorption and the like in the surface regions, while the abrasion tests, /53

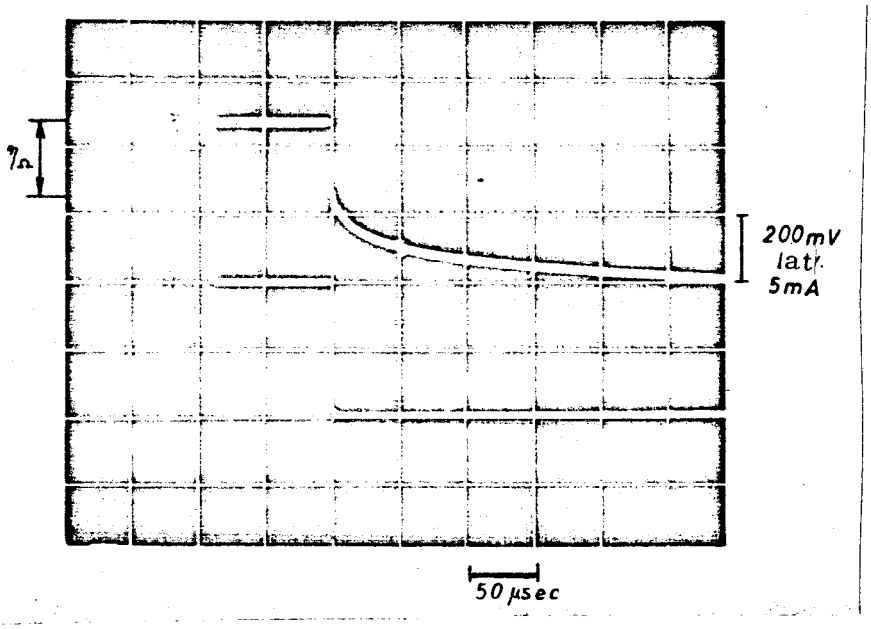

Fig. 14. Calibration Oscillogram. Copper Cathode in 2n-H_2SO_4 at 23° C; High Flux Density ($j \approx 2$ A/cm^2). Recorded After Interruption of Abrasion. Very Rapid Drop in Overtension Amounting to an Ohmic Component of η_Ω.

on the other hand, give measurement values for the actual contact material. The abrasion method is also probably a valuable method of investigation for studying formation processes, the interfacial quality of electrodes, and the kinetics of double layer formation. In this regard, experiments with pretreated contacts and the study of the behavior of the resting values with time as well as the periodicity of the abrasion with alternating abrasion frequency promise interesting results.

3c. Poisoning of the Electrodes and the Problem of Reproducibility

The abrasion tests show that the obtaining of reproducible overtensions is less dependent on the extreme purity of the substrate than on the use of electrode surfaces which are as fresh as possible and free of a coating. The poisoning of the surfaces by electrolytes, caused by adsorption of impurities, obviously

necessitates a certain period of accumulation; hence, if the surface is renewed sufficiently rapidly, even relatively high impurity concentrations in the substrate will not produce any significant change in the overtension. With this in mind, the relationships were studied to test the reliability of the measured values and the effect of poisoning in several experiments [74]. The question arose of how the overtension would behave following interruption of the abrasion with different amounts of impurities in the electrolytes. We were also interested in determining whether (and to what degree) large amounts of impurities would have an influence on the overtension values in abrasion measurements. Therefore, in these experiments increasing amounts of the strong electrode poison As_2O_3 were added to the electrolyte and the overtension was observed during the abrasion, after its interruption, and during renewed abrasion. Some representative results are shown in Figure 15.

These results show that in fact the overtension is altered even in abraded electrodes at relatively high poison concentrations. From this we also see that the measurements with nonpoisoned electrolytes can also show "poisoned" values on occasion [23]. It was also determined that after the abrasion is interrupted, even when electrolytes are used which have not been especially purified (but not artificially poisoned either), a period of at least several seconds is required until a noticeable change in the overtension is observed[24]; even after several minutes, it still does not amount to more than 10 to 20 mV. (Cf. also the resting value segment in Fig. 12). Hence, the abrasion can be interrupted for a relatively long period of time. Therefore we see that abrasion tests, even under simple purity conditions, not only yield highly reproducible results, but also provide unfalsified data which are characteristic for the electrode material. /54

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[23] The constancy of the overtension with time in the abrasion measurements was confirmed in a few long-term tests.

[24] According to Bockris and Conway [43], certain poisons (primarily As_2O_3) even in concentrations of 10^{-10} moles/liter, can falsify the overtension values to a considerable extent. See also [82,83], and the literature contained in these papers.

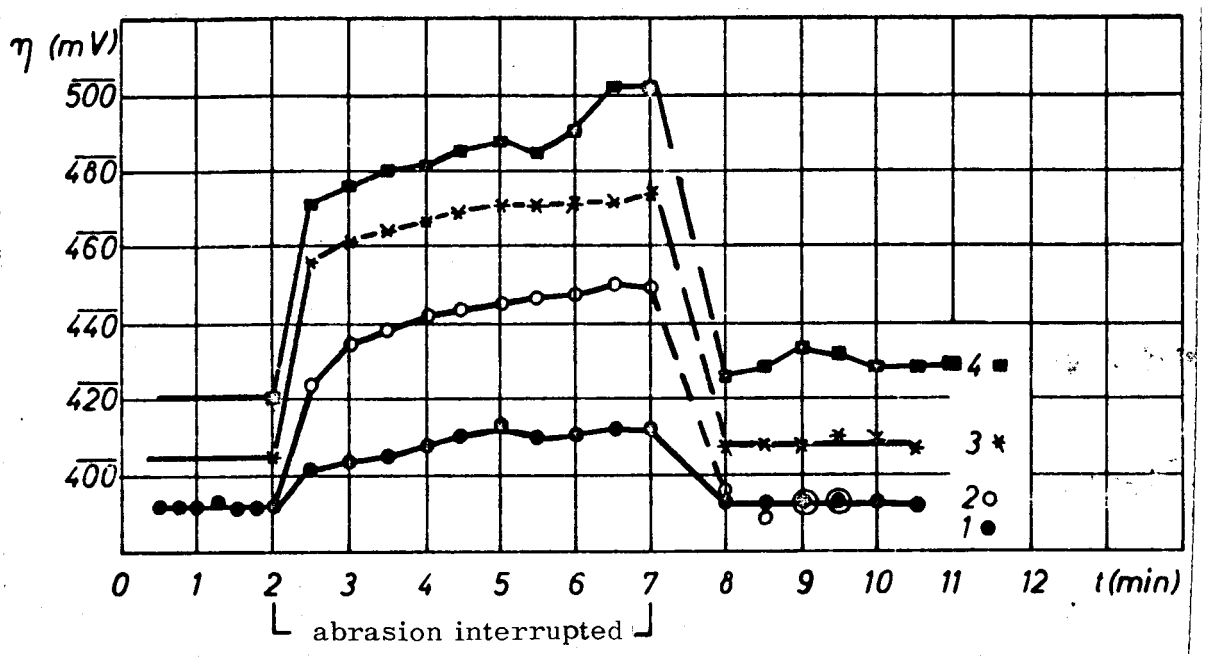

Fig. 15. Poisoning Tests. Gold Cathode in 2n-H_2SO_4 (~150 ml); Current I = 0.1 mA (j ≈ 0.01 A cm^2). Addition of Poison (0.01m-As_2O_3-Solution); (1) None Added; (2) Five Drops; (3) One ml; (4) 2 ml.

PART B

HYDROGEN OVERTENSION IN VARIOUS METALS AND ALLOYS

CHAPTER VII

EXPERIMENTAL SYSTEMS

In the following sections, we will describe the results which /55
we have obtained thus far in our comparison measurements of overtension in metals and alloys. Using a comprehensive program of investigation, we are endeavoring to use investigations of this type to determine the relationships between the overtension and the material properties of contacts, as well as to learn about the nature and influence of the contact-chemical parameters. Such knowledge will be of value to an understanding of the contact behavior of metal systems.

In setting up our program of investigation, we operated on the basis of the theory that the comparison systems used for obtaining concrete and definite relationships increase in suitability in direct proportion to the extent to which their components resemble one another in design and characteristics.

There are two basic types of metallic systems, which fit the above requirements to a satisfactory degree: the groups of analogous metals and the homogeneous alloys. As far as the problems of contact chemistry are concerned, there are two basic heuristic possibilities according to which the following division can be made:

(a) Systems in which individual material parameters undergo separately a variation which is as extensive and continuous as possible. In particular, such systems permit investigation of the influence of individual effective parameters. They are usually to be found in certain homogeneous substitution alloys; in these alloys, the electronic properties can be varied as desired by adding other components while retaining the basic structure of the original metal (cf. Chapter II.2a). This category can be subdivided further as follows:

(α) The α-phases of the Hume-Rothery alloys (e.g., Cu-Zn, Ag-Cd, Au-Cd). In this case, the addition of materials causes filling of the conduction bands with electrons.

(β) The alloys of the Ib-metals with the d-metals (Cu-Ni, Ag-Pd, Au-Pd), which are homogeneous at all mixture ratios. In this case, the addition of the d-metals reduces the electron population. These alloys are also of interest in the interpretation of the d-states. /56

(b) Systems of homologous substances, whose investigation is especially interesting precisely because their representatives are completely uniform and therefore should show a corresponding behavior, while any differences that might occur would lead on the one hand to a refinement of the series and on the other hand to the posing of completely new problems. These systems include the following:

(α) The groups of homologous metals (e.g., Cu, Ag, Au).
(β) The homogeneous alloys of homologous metals (e.g., Cu-Au, Ag-Au).

In the following sections, we shall be discussing the overtension studies of the Ib-metals and their Hume-Rothery alloys which we have conducted thus far. The following alloy systems lend themselves to more detailed study because of the sufficient width of their α-phase regions:

Cu	Ag	Au
Cu-Zn	Ag-Cd	Au-Zn
Cu-Al	Ag-In	Au-Cd
Cu-Ga	Ag-Sn	Au-In
Cu-Ge	Ag-Sb	Au-Sn
Cu-As		

The discussions deal primarily with the findings for the copper and gold groups, because the latter have already been studied in detail with the abrasion method. In the case of the silver group, with which we began our investigations and therefore initially used the method which had previously been conventional, we are presently lacking the more detailed and useful measurements which are required for analyses corresponding to the viewpoint which has been developed above.

The cathode metals and alloys were obtained either in the form of wires (diameter = 0.50 mm) from the firm of Heraeus in Hanau or manufactured by ourselves from the components (silver alloys)[25]. The degree of purity of the samples in all cases was at least 99.99%. The homogeneity of the alloys was tested by x-ray analysis.

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[25] For details on the preparation of the silver alloys, see [69].

The copper and gold alloys which were used are discussed separately in Tables V and VI. The "electron concentrations" EC are given to characterize their electronic relationships. These are calculated as formal conduction electron numbers per atom by the formula: /57

$$EC = 1 + (n_X - 1)\gamma_X,$$

in which n_X is the group valence and γ_X is the mole fraction of the added metal.

TABLE V

COPPER ALLOYS (α-PHASES)

alloy	addition atom-%	electron concentration EC
Cu	-	1
Cu-Zn I	5	1,05
II	10	1,10
III	15	1,15
IV	20	1,20
V	25	1,25
Cu-Al I	5	1,10
II	10	1,20
III	15	1,30
Cu-Ga I	5	1,10
II	10	1,20
III	15	1,30
Cu-Ge I	2	1,06
II	4	1,12
III	6	1,18
Cu-As I	2	1,08
II	4	1,16
III	5	1,20

TABLE VI

GOLD ALLOYS (α-PHASES)

/58

alloy	addition atom-%	electron concentration EC
Au	-	1
Au-Zn I	5	1,05
II	10	1,10
Au-Cd I	5	1,05
II	10	1,10
III	15	1,15
Au-In I	3	1,06
II	6	1,12
Au-Sn I	2	1,06
II	4	1,12

CHAPTER VIII

OVERTENSION FINDINGS

/59

The measurement data discussed in the following, unless otherwise indicated, were obtained by the abrasion method. The electrolyte was always analytically pure 2n-sulfuric acid. Repurified hydrogen from the firm of Linde was used for bubbling over the reference electrode and through the experimental electrolyte.

1. Remarks on Experimental Procedure[26]

The abrasion tests were usually carried out in open electrolysis cells made of glass. The following were submerged in the electrolyte: the test cathode, the ruby scraper (both imbedded in plexiglas and araldite), a Luggin lifter for the reference electrode, a hydrogen inlet tube, a precision thermometer for determining the electrolyte temperature, and the platinum anode which was mounted in a fritted container to guard it against anodic reaction products from the cathode.

The electrolysis cell was placed in a water bath, which ensured constant temperature within 0.2° C.

As the reference electrode, we used a platinum-hydrogen electrode (normal hydrogen electrode), filled with the test electrolyte, whose potential was measured in each experiment by matching it against a calomel electrode; the cell potentials obtained were in good agreement with the latest values given by H. Chateau [84]. The hydrogen electrodes proved to be extraordinarily constant.

The overtensions were measured with a high-resistance VTVM (Knick D.C. Millivoltmeter mV 21; internal resistance approximately equal to 10^8 Ω). For suppression of stray currents, all circuit elements were placed in a grounded metal box and shielded coaxial cables were used for the leads. The cathodes and shields were also grounded.

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[26] Cf. also Chapters III and VI. Further details are given in [70a, 78,79].

The electrolysis current was provided by a power supply (Gossen, constant from 0.5-15 V) or a battery. The current was adjusted with voltage dividers and variable resistors. The current intensities were also measured with a vacuum tube instrument (Hewlett-Packard Type 412A). The flux densities were calculated on the basis of the geometrical cathode surfaces.

In each experiment, stationary current-potential curves were always recorded in a downward and upward measurement in the flux-density range $j \approx 10^{-3}$ to 10 A/cm^2. The overtensions corrected for the ohmic components yielded very good Tafel curves in all experiments. /60

The overtension values listed are averages of at least five independent experimental measurements.

1a. Overtension Determination at Different Temperatures. Temperature Coefficient of $\bar{\bar{\varepsilon}}$.

To determine the true overtensions, the cathode potential must be based on the equilibrium potential of a hydrogen electrode under analogous conditions (electrolyte and temperature). As far as the electrolyte conditions are concerned, this prerequisite was completely satisfied in our experimental setup. With regard to temperature, we always ensured that the reference electrode was kept at room temperature in all the experiments when it was outside of the electrolysis cell and its water bath, and that the potential values for the corresponding experimental temperature were adjusted with the aid of a suitably obtained calibration curve. From the standpoint of apparatus, this procedure is much simpler and more reliable.

The correction function, i.e., the temperature dependence of the reversible normal hydrogen electrode, was determined with the setup shown in Figure 16a, as the potential difference between two uniform platinum hydrogen electrodes; the constant temperature T_0 was 25° C.

The measured value $\Delta\varepsilon_{common}$ is composed of the difference $\Delta\bar{\bar{\varepsilon}} = \bar{\bar{\varepsilon}}(T) - \bar{\bar{\varepsilon}}(T_0)$ between the equilibrium electrode potentials and the very small potential differences in the transition zones between T_0 and T. Hence, $\Delta\varepsilon_{common}$ corresponds directly to the amount by which the measured overtensions must be reduced when the temperature of the reference electrode is 25° C in the measurements. The correction function is shown in Figure 16b; it is practically linear in the measurement range

$$\frac{\partial \Delta\varepsilon_{common}}{\partial T} = + 0.5 \text{ mV/deg.}$$

The empirical function gives us the approximate value of the

temperature coefficient of the equilibrium potential of the normal platinum hydrogen electrode:

$$\frac{\partial \bar{\varepsilon}_{Pt}}{\partial T} = +\,0{,}5\ \text{mV/deg}.$$

H_2-electrodes. Electrolyte: 1m-H_2SO_4

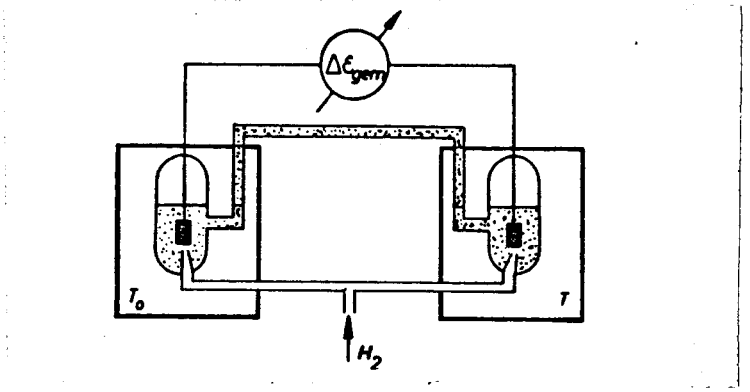

Fig. 16a. Arrangement for Temperature Calibration of Hydrogen Reference Electrodes.

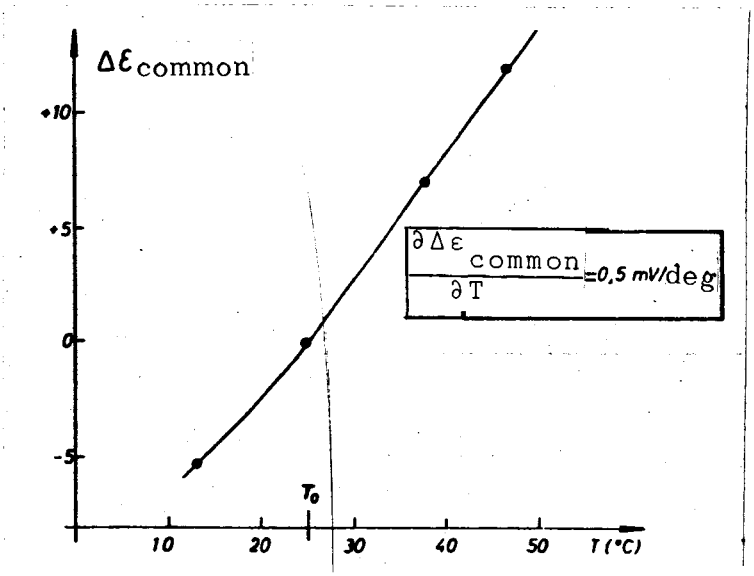

Fig. 16b. Temperature Dependence of the Potential of the Hydrogen Normal Electrode.

In view of the thermodynamic relationships /61

$$\frac{F\,\partial\bar{\varepsilon}_{Pt}}{T} = \frac{\partial \Delta G_{Pt}}{\partial T} = -\Delta S_{Pt}$$

the approximate amounts for the temperature coefficient of the free reaction enthalpy or reaction entropy of the electrode process can be calculated as follows:

$$\frac{\partial \Delta G_{Pt}}{\partial T} = -\Delta S_{Pt} = +11{,}5\ \text{cal/ mole deg.}$$

For the Peltier heats, this gives us a figure of approximately 3.5 kcal/mole at 300° K, which appears to be quite accurate since the data given in the literature indicate that the Peltier heats should be on the order of 10 kcal/mole [44, p. 104].

2. Measurement Data (Current-Potential Curves)

2a. Copper and Gold

The overtension parameters for copper and gold electrodes are listed in Table VII; a great many measurements were made with these two metals, whose results were in complete agreement with the figures listed in the Table.

TABLE VII

OVERTENSION PARAMETERS FOR COPPER AND GOLD

metal	temp. (°C)	Tafel constants $-a_T$ (mV)	Tafel constants b (mV)	α	$-\log j_0$
Cu	13	769 ± 4	102 ± 1	0,554	7,53 ± 0,06
	23	761 4	105 1,5	557	7,25 7
	35	739 4	110 1	555	6,74 9
	48	737 5	116 1	548	6,34 7
Au	12,5	625 ± 4	100 ± 0,5	0,569	6,25 ± 0,03
	22,5	603 2	103 0,5	569	5,86 3
	35,5	581 3	106,5 0,5	574	5,46 5
	49,0	566 3	112 0,5	569	5,06 2

2b. Copper Alloys

Some peculiar features were observed in the measurements of /62
the copper-zinc alloys: a number of the current-potential curves showed a parallel shift toward higher overtensions in the upper measurement ranges, which usually showed up at $\eta \approx -650$ mV. The

measured values obtained for both segments with rising and falling flux density were in complete agreement (Fig. 17). The effects may be explained by the dissociation of Zn^{++}-ions, which are dissolved out of particles of the alloy removed from the cathodes during abrasion. Experiments with copper cathodes, in which zinc sulfate had been added to the electrolyte, showed at least the same phenomena (Fig. 18), which (together with the low acid resistance of this alloy) is highly favorable to such an interpretation. No further attempts were made to determine the overtension characteristics of the Cu-Zn alloys by special measurement methods. The measurement data for the other copper alloys are listed in Table VIII.

Since the overtension behavior of the copper-arsenic alloys differed markedly from that of the other alloys and arsenic is known to be a strong electrode poison, special experiments were devoted to the problem of whether the measurements on these alloys were falsified by the influence of arsenic dissolved in the electrolyte. Increasing amounts of As_2O_3 were added during measurements with copper cathodes. The experiments showed that small amounts of poison ($<10^{-6}$ mole/ liter) had no effect on the overtension, and that higher As concentrations caused an increase in the overtension[27].

These findings show that the measurement data for the copper-arsenic alloys have not been falsified: in the first place, if we estimate that a maximum of 10^{-7} moles of arsenic could enter the electrolyte during a measurement series, we have an amount which lies below the limit of influence. In the second place, the overtension parameters of arsenic alloys are definitely below those for copper, while on the other hand, in measurements with poisoned electrolytes, higher (more negative) values were always found.

2c. Gold Alloys

Table IX shows the results for these alloys.

2d. Silver and Silver Alloys

As we have already noted, this group was the first one studied, so that the less accurate older method was used in investigating it[28]. We will forego a discussion of these measurement data in detail now, because no findings for the temperature dependence are available.

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[27] These findings agree with the corresponding experiments on gold cathodes, described earlier.

[28] These investigations were published in [69] with a detailed description of the methodology of the old method.

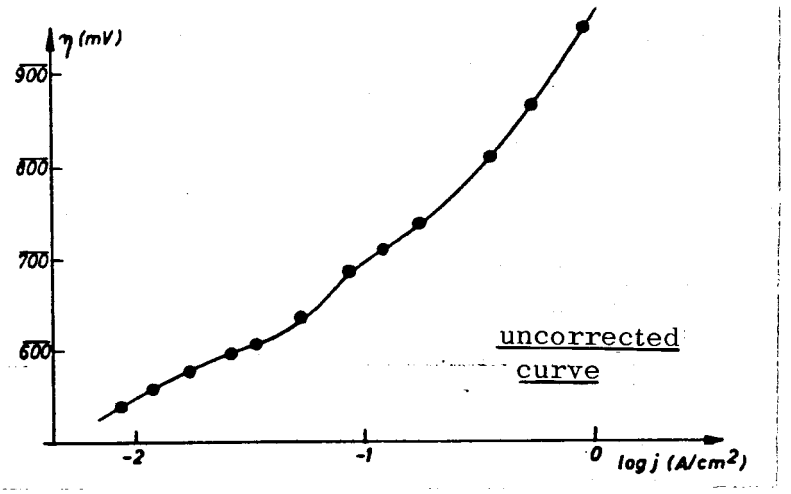

Fig. 17. Current-Potential Curve for a Cu-Zn Cathode (23° C).

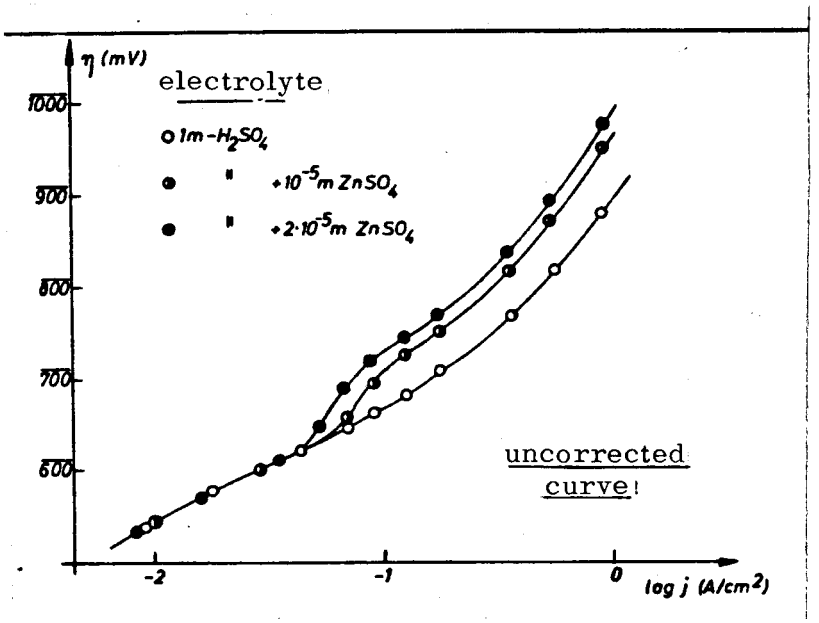

Fig. 18. Current-Potential Curves for a Copper Cathode, With Addition of Zn^{++}-Ions to the Electrolyte.

TABLE VIII. OVERTENSION PARAMETERS FOR COPPER ALLOYS

alloy	temp. (°C)	Tafel constants $-a_T$ (mV)	Tafel constants b (mV)	α	$-\log j_0$
Cu-Al I	13	771 ± 2	101 ± 1	0,562	7,65 ± 0,04
	22	762 2	104 1	559	7,29 2
	35	733 2	106 0,5	575	6,91 4
	48	704 4	110 0,5	578	6,40 3
Cu-Al II	13	768 ± 3	102 ± 1	0,555	7,53 ± 0,02
	22	755 5	104 1	559	7,19 8
	35	733 1	107 0,5	570	6,85 2
	48	708 4	109 0,5	583	6,48 2
Cu-Al III	13	768 ± 2	105 ± 1	0,539	7,30 ± 0,05
	22	761 3	106 1	549	7,14 9
	35	737 1	107 0,5	567	6,86 2
	48	712 1	109 0,5	583	6,53 3
Cu-Ga I	13	782 ± 1	100 ± 0,5	0,564	7,79 ± 0,04
	22	776 3	104 1	559	7,42 6
	35	756 2	108 0,5	565	7,01 2
	48	727 2	109 1	580	6,64 4
Cu-Ga II	13	794 ± 3	107 ± 0,5	0,526	7,35 ± 0,06
	22	772 1	109 1	536	7,08 6
	35	764 6	110 0,5	555	6,95 4
	48	732 5	113 1	560	6,46 9
Cu-Ga III	13	795 ± 3	109 ± 1	0,522	7,33 ± 0,04
	22	793 1	109 0,5	536	7,26 2
	35	770 1	110 1	555	6,99 3
	48	738 3	111 1	572	6,65 3

TABLE VIII. (Continued)

alloy	temp. (°C)	Tafel constants $-a_T$ (mV)	Tafel constants b (mV)	α	$-\log j_0$
Cu-Ge I	13	779 ± 4	104 ± 0,5	0,541	7,45 ± 0,06
	22	766 2	105 0,5	554	7,26 3
	35	746 4	108 1	562	6,87 6
	48	720 2	110 0,5	578	6,53 2
Cu-Ge II	13	779 ± 3	104 ± 1	0,545	7,49 ± 0,05
	22	771 1	106 0,5	551	7,30 4
	35	752 1	107 0,5	570	7,03 2
	48	724 4	108 1	585	6,67 6
Cu-Ge III	13	773 ± 5	105 ± 1	0,539	7,37 ± 0,07
	22	759 3	107 0,5	543	7,07 3
	35	744 2	109 0,5	560	6,82 6
	48	723 3	110 1	575	6,53 5
Cu-As I	13	740 ± 4	108 ± 1	0,524	6,87 ± 0,05
	22	712 4	110	531	6,47 4
	35	695 1	110 0,5	555	6,32 3
	48	672 6	115 1	550	5,82 5
Cu-As II	13	760 ± 4	111 ± 1	0,510	6,84 ± 0,04
	22	743 9	111 0,5	526	6,69 7
	35	726 4	114 0,5	535	6,37 3
	48	697 3	116 0,5	547	6,02 7
Cu-As III	13	751 ± 3	110	0,515	6,83 ± 0,02
	22	727 4	111 ± 1	526	6,55 4
	35	725 3	114 1	535	6,35 3
	48	691 4	117 0,5	540	5,88 4

TABLE IX. OVERTENSION PARAMETERS FOR GOLD ALLOYS

/65

alloy	temp. (°C)	Tafel constants $-a_T$ (mV)	b (mV)	α	$-\log j_0$
Au-Zn I	12,5	616 ± 3	98 ± 0,5	0,578	6,30 ± 0,03
	22,5	608 3	101,5 1	577	6,00 2
	35,5	591 3,5	105,5	580	5,60 3
	49,0	556 2	107 1	595	5,20 4
Au-Zn II	12,5	619 ± 5	102 0,5	0,557	6,07 0,07
	22,5	603 5	104 1	564	5,79 4
	35,5	576 5	105 0,5	583	5,49 6
	49,0	554 7	107 1	595	5,12 6
Au-Cd I	12,5	612 ± 1,5	107 ± 1	0,527	5,69 0,02
	22,5	597 2	110 0,5	533	5,42 2
	35,5	569 6	111,5 0,5	548	5,11 6
	49,0	540 3	114,5 1	557	4,72 4
Au-Cd II	12,5	603 ± 1,5	110,5 ± 0.5	0,512	5,46 ± 0.02
	22,5	581 4	113 0,5	518	5,15 3
	35,5	553 3	115 1	532	4,82 5
	49,0	524 4	117 0,5	545	4,47 2
Au-Cd III	12,5	592 ± 2	104 ± 1	0,544	5,68 ± 0,02
	22,5	572 3.5	106 0.5	553	5,39 4
	35,5	540 0,5	107,5 0,5	569	5.03 1
	49,0	518 6	110 0,5	579	4,67 6
Au-In I	12.5	620 ± 5	104 ± 0,5	0,544	5.96 ± 0.06
	22.5	607 3	111 0,5	528	5.47 2
	35,5	585 4	114 0.5	537	5,13 4
	49,0	559 2	117 0,5	545	4,79 1
Au-In II	12,5	627 ± 2	107 ± 0,5	0,529	5,87 ± 0,04
	22,5	609 5	109,5 0,5	535	5,56 3
	35,5	587 3	112,5 1	544	5,22 3
	49,0	562 3	115 0,5	554	4,88 3
Au-Sn I	12.5	623 ± 2	105 ± 0,5	0,539	5,94 ± 0,03
	22,5	611 2,5	110 0,5	533	5,54 2
	35,5	587 2,5	111,5 0,5	548	5,26 2
	49,0	558 2	113 0,5	564	4,93 2
Au-Sn II	12,5	614 ± 1,5	107 ± 0,5	0,529	5,74 ± 0,02
	22,5	600 1	111 0,5	528	5,41 2
	35,5	582 5	112 0,5	546	5,19 4
	49,0	547 5	113 1	564	4,87 2

/66

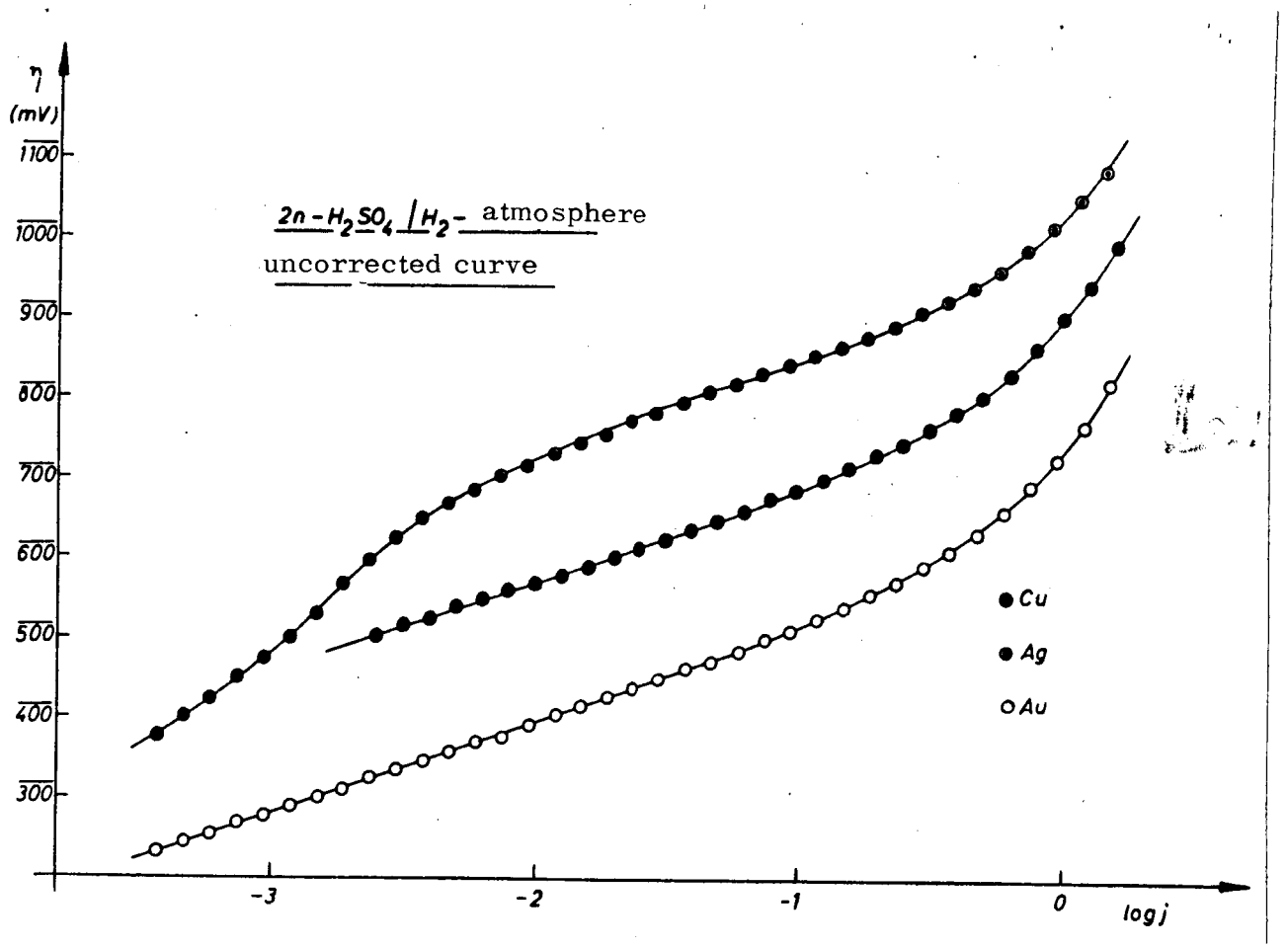

Fig. 19. Current-Potential Curves for Copper, Silver, and Gold at 23° C. (The Somewhat Higher Slope of the Gold Curve Here Was Caused by the Measurement Technique and is Without Significance).

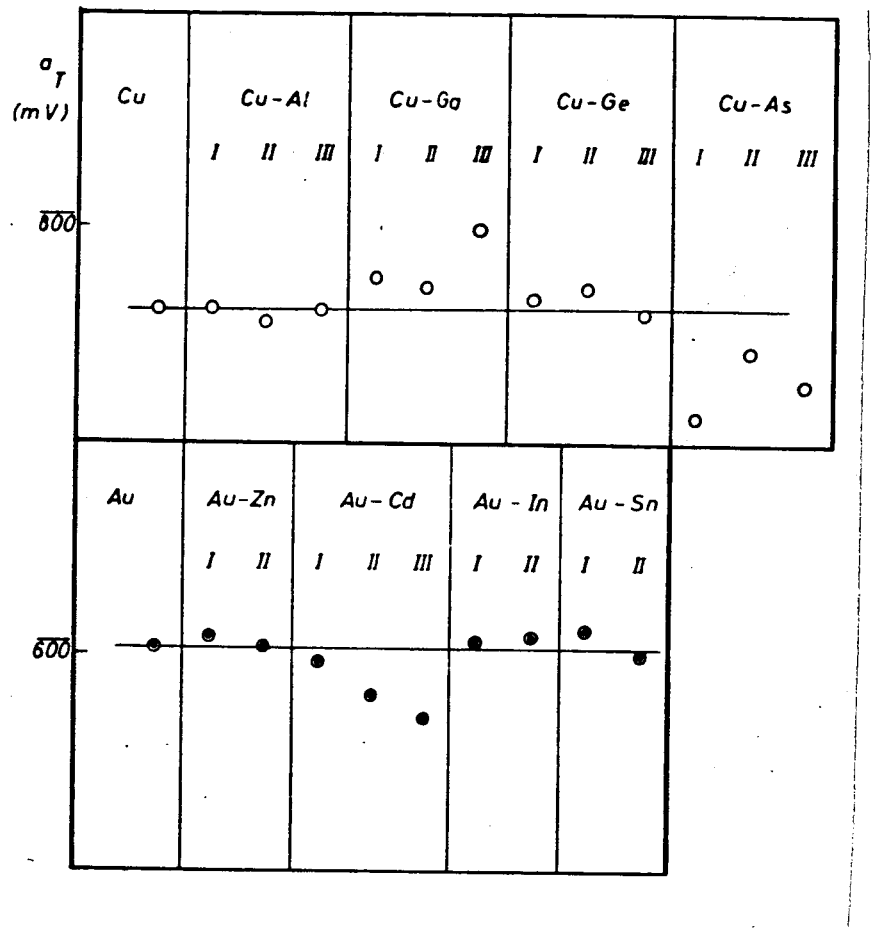

Fig. 20. Characteristic Tafel Constants a_T for Copper and Gold Alloys (α-Phases) at Room Temperature.

In the meanwhile, we have begun abrasion experiments with silver cathodes; they are generally very interesting because they reveal special relationships for this metal, whose detailed study promises to bring up some interesting new problems. The abrasion tests yield current-potential curves which differ in position and shape from the normal pattern for the homologous series Cu-Ag-Au (Fig. 19). In addition, because silver was the only metal studied by the old method, there are differences in the measurement data for abraded and unabraded electrodes which also show up as a dependence on the abrasion frequency. /67

These findings indicate that there may be a cathode system in silver in which a change in the mechanism occurs within the measurement range. It is possible that the Volmer step determines the kinetics in one partial range and the Horiuti step determines the kinetics in another; between these there would be a transition zone in which no one partial step would be critical. There is no simple Tafel equation for this transition region, but only the complex common current-potential relationship discussed in Chapter III.3. In the case of a slow Volmer step, it is completely possible that the periodic reformation of the double layer requires longer times in the abrasion process, which lie within the order of magnitude of the abrasion periods. In such a case, however, the measured values are functions of the abrasion frequency.

2e. Characteristic Overtensions at a Given Temperature

It was mentioned in Chapter V that no definite data could be obtained by using the earlier method of comparison overtension studies, which was limited to measurements at one temperature. As an example illustrating this shortcoming, we have plotted in Figure 20 the characteristic overtension values $a_T(j = 1\ A/cm^2$ of various types of cathodes for $T \approx 20^\circ$ C [29]. In the case of the copper and gold groups, we obtain the unsystematic relation ship already mentioned in Chapter V.1 as well as the overtension behavior which is evidently independent of the cathode composition, while in the case of the silver alloys, regular relationships appear to be the rule.

3. Kinetic Parameters

3a. Experimental Frequency Factors and Activation Energies

For all the systems investigated, the electrode reaction follows an Arrhenius curve. A few representative log j_0 - 1/T diagrams are shown in Figures 21 and 22; for the sake of clarity, the Arrhenius curves have been plotted separately for the copper alloys. /68

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[29] Similar results are obtained at the other experimental temperatures.

The experimental (logarithmic) frequency factors log A and activation energies q of all the systems, obtained from the diagrams, are shown in Table X.

3b. θ-Relationships

As we know, an approximately linear relationship is frequently found empirically between the activation energies and frequency factors in the case of a reaction measured on different contacts or on contacts that have been prepared in different ways. We then speak of the fulfillment of a θ-rule or a compensation effect[30]; In this case, an increase in the frequency factor is related to a similar increase in the activation energy: the former increases the reaction rate while the latter decreases it, so that a certain mutual compensation results with respect to the gross activity. In the presence of a θ-relationship, there appears to be a characteristic temperature θ at which the Arrhenius curves of the different systems intersect, indicating that the reaction rates are equal. The linear relationship between ln A and q is expressed as follows:

$$\ln A = \frac{1}{R\Theta} q + \text{const.}$$

Corresponding plots of our results (Fig. 23 and 24) show that our reaction systems satisfy θ-relationships with quite satisfactory accuracy. As characteristic temperatures, we find the following:

$\Theta = 303^{\circ}K = 30^{\circ}C$	(Copper Group)
$\Theta = 317^{\circ}K = 44^{\circ}C$	(Gold Group)

According to Cremer and Schwab [85, 86], the θ-value should correspond roughly to the preparation temperature of the corresponding contact.

We do not wish to assign too much importance to the θ-values found above, since their determination is not extremely accurate and was undertaken in a formal manner; i.e., we cannot exclude the possibility that the effect lies partly within the error. However, it seems remarkable that the findings also satisfy these prerequisites quantitatively to an astonishing degree, since in our case the preparation of the surfaces was accomplished by abrasion in the temperature range between 10-50° C.

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30 For further information regarding the θ-rule and its theoretical basis, see [38] especially p. 140 ff, as well as the original literature cited in this work.

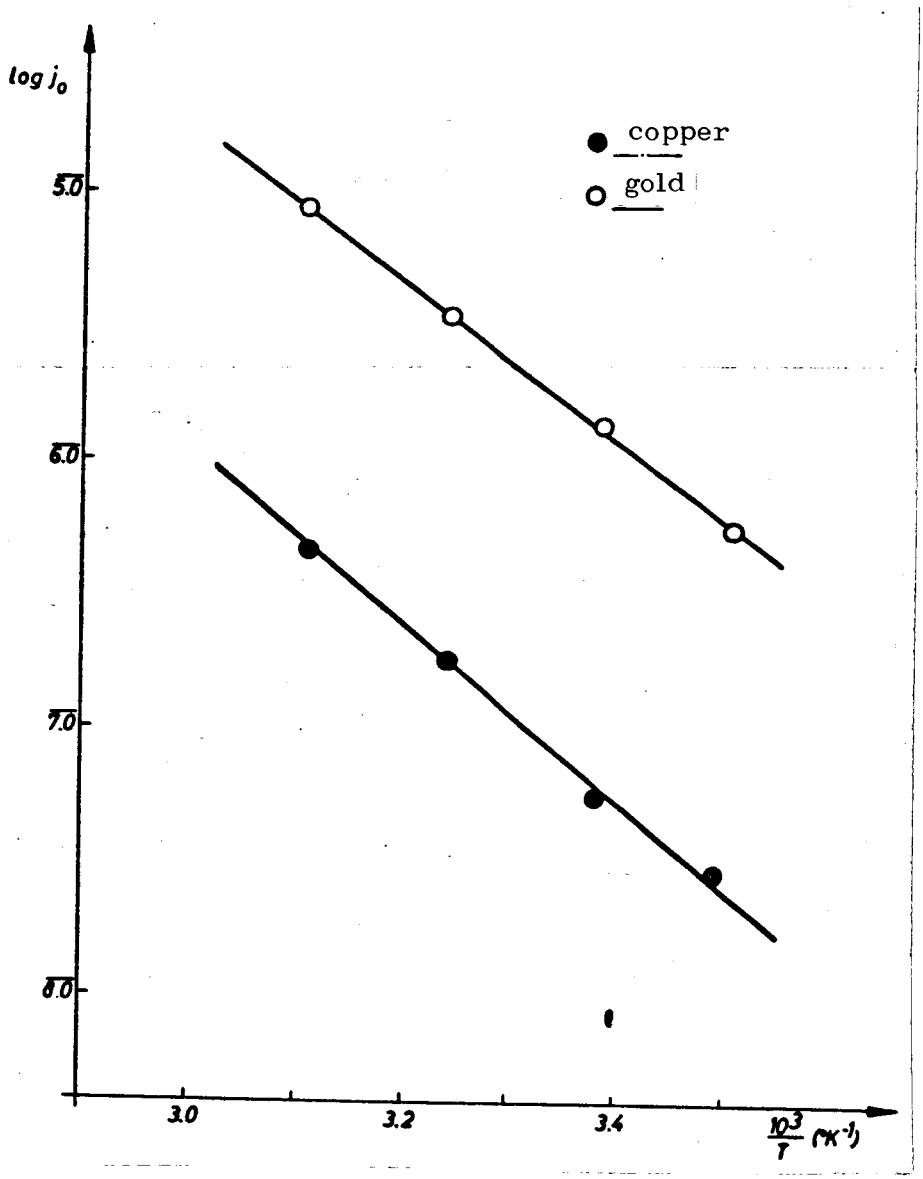


Fig. 21. Arrhenius Diagrams of Cathodic Hydrogen Dissociation on Copper and Gold.

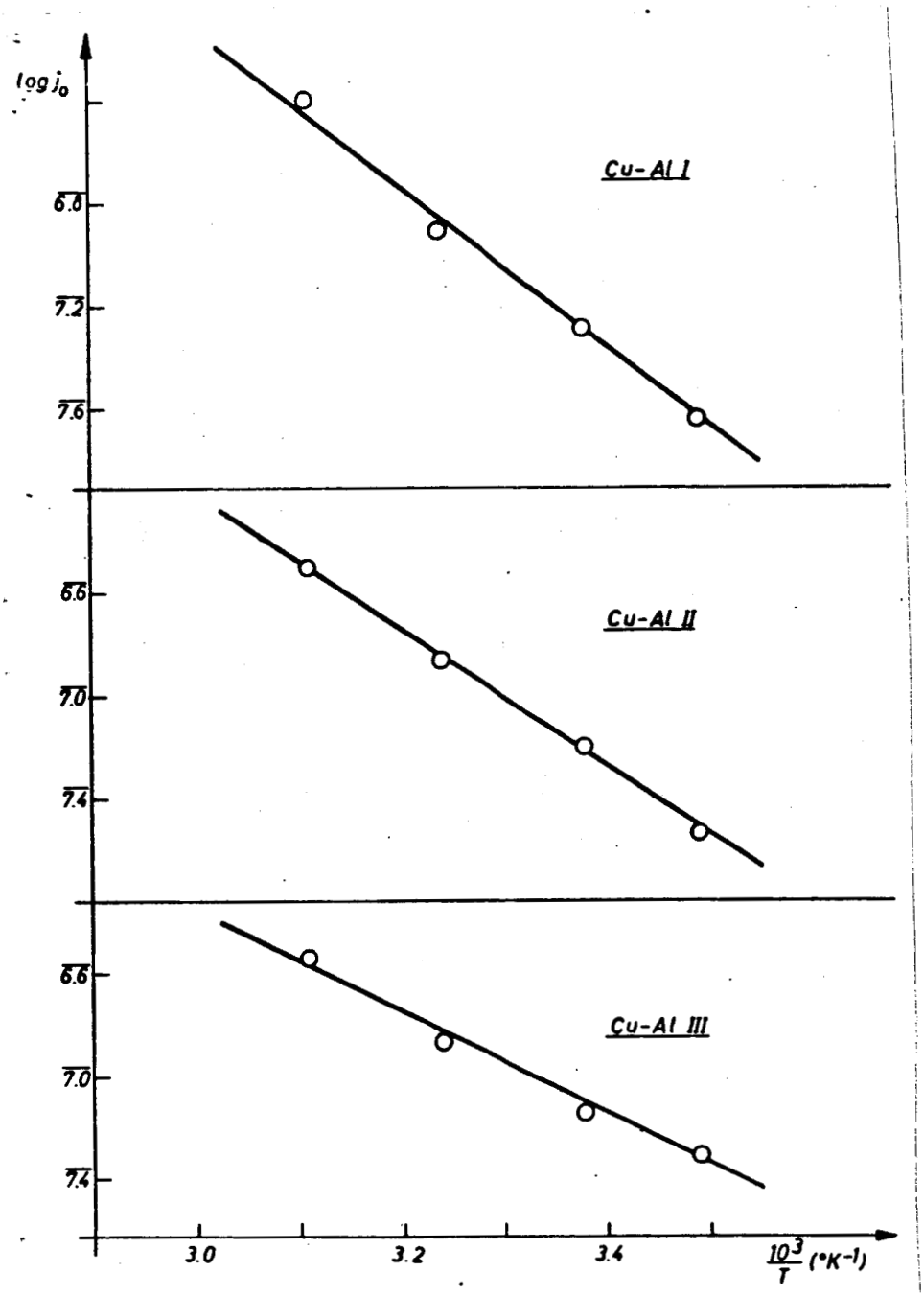


Fig. 22. Arrhenius Diagrams for Copper-Aluminum Cathodes.

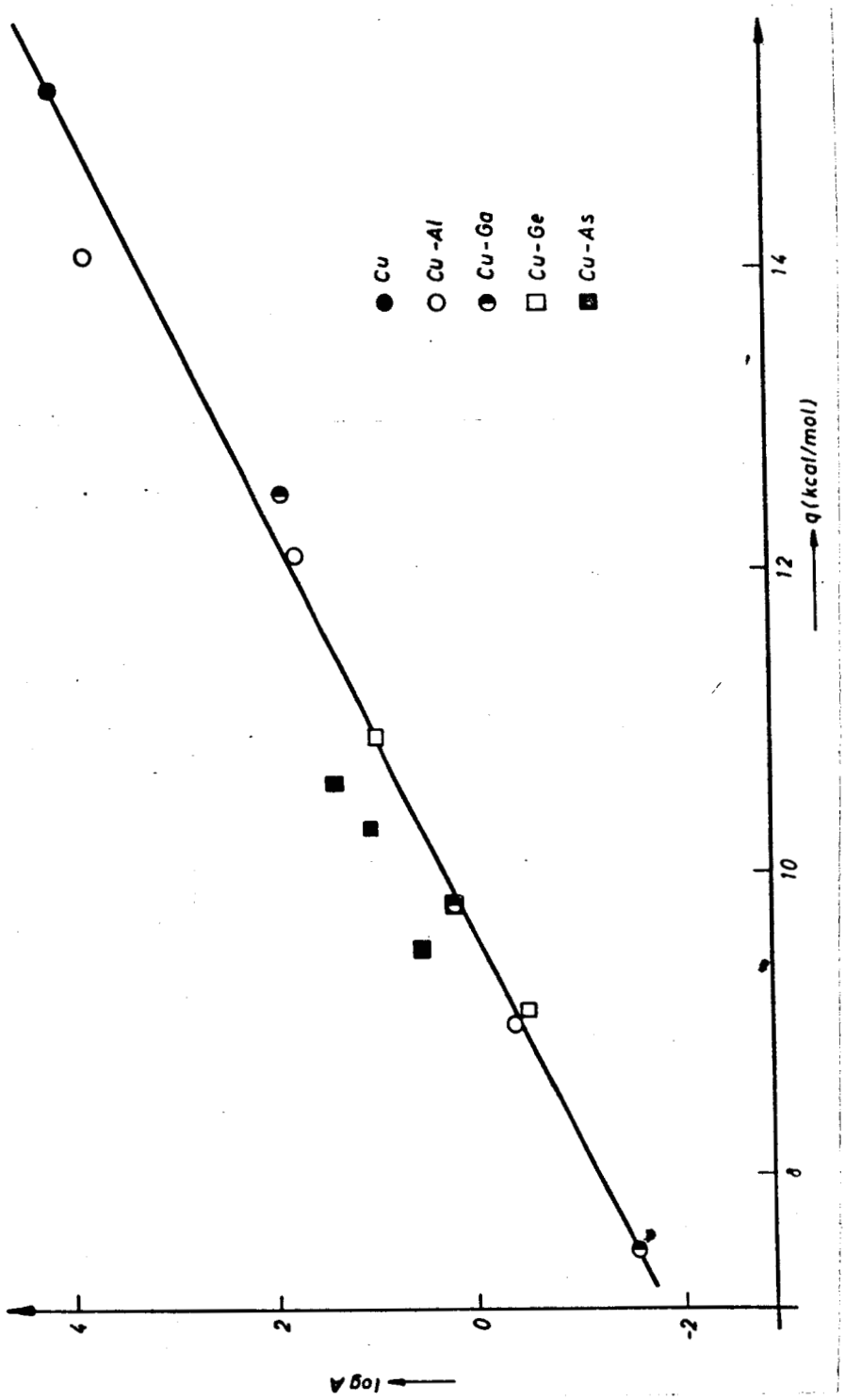


Fig. 23. Log A-q Diagram (θ-Curve) for Copper Alloys.

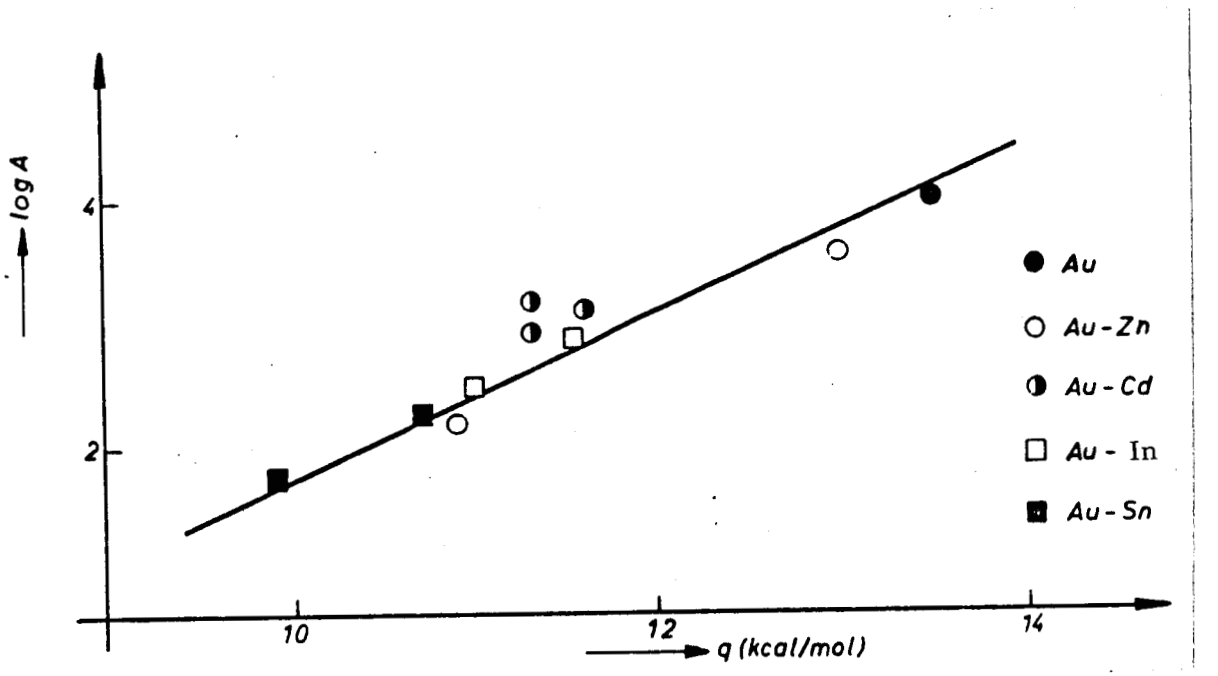


Fig. 24. Log A-q Diagram (θ-Curve) for Gold Alloys.

TABLE X. EXPERIMENTAL ACTIVATION ENERGIES AND FREQUENCY FACTORS

/69

	cathode		q (kcal/Mol)	log A
a) copper group				
	Cu		15,2	4,06
	Cu-Al	I	14,1	3,18
		II	12,1	1,75
		III	9,0	-0,39
	Cu-Ga	I	12,5	1,86
		II	9,8	0,18
		III	7,5	-1,55
	Cu-Ge	I	10,9	0,92
		II	9,1	-0,5
		III	9,8	0,17
	Cu-As	I	10,6	1,36
		II	10,3	1,01
		III	9,5	0,53
b) gold group				
	Au		13,5	4,00
	Au-Zn	I	13,0	3,55
		II	10,9	2,20
	Au-Cd	I	11,6	3,10
		II	11,3	3,16
		III	11,3	2,94
	Au-In	I	11,4	2,86
		II	11,0	2,49
	Au-Sn	I	10,7	2,26
		II	9,9	1,76

These relationships provide an explanation for the lack of dependence of the overtension curve on the cathode material, which was first observed only in the experiments conducted at room temperature but was very difficult to understand. The theory that this independence might be simulated by compensation effects has proven to be correct. /70

4. Discussion

4a. Summary of the Findings

Investigations have led to the following conclusions:

(1) Measurements at a given temperature do not provide a clear and definite picture of the dependence of the overtension upon the cathode material.

(2) The temperature dependence of the electrode reaction, which always satisfies an Arrhenius equation, reveals (on the other hand) regular differences in the behavior of various cathode alloys. Smaller experimental activation energies were found for both the copper and gold groups than for the pure basic metals.

(3) In addition, the activation energies decrease within the alloys with increasing amounts of additive.

(4) The kinetic parameters (A, q) obey the θ-rule.

(5) The Tafel slopes of all measured current-potential curves correspond to the theoretical value.

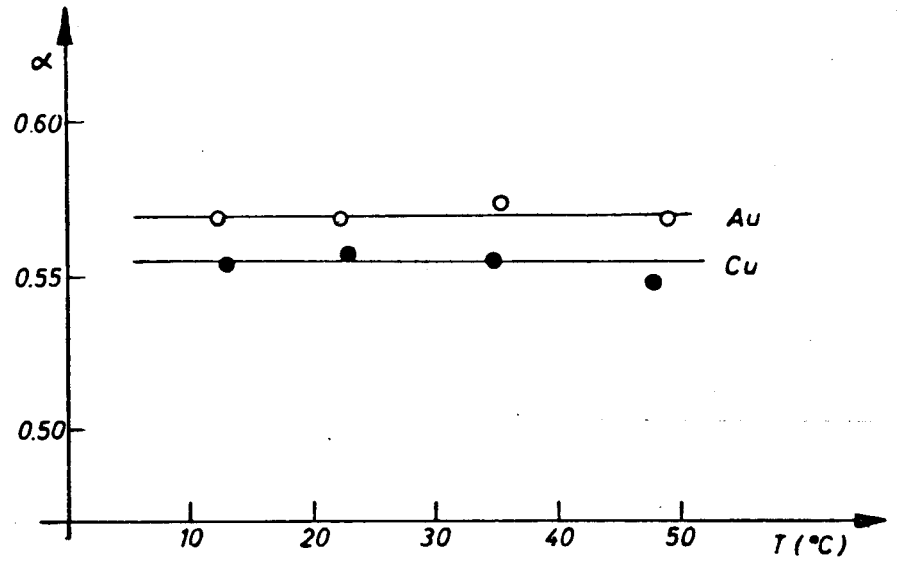
$$b = \frac{2.3\ RT}{\alpha T}$$

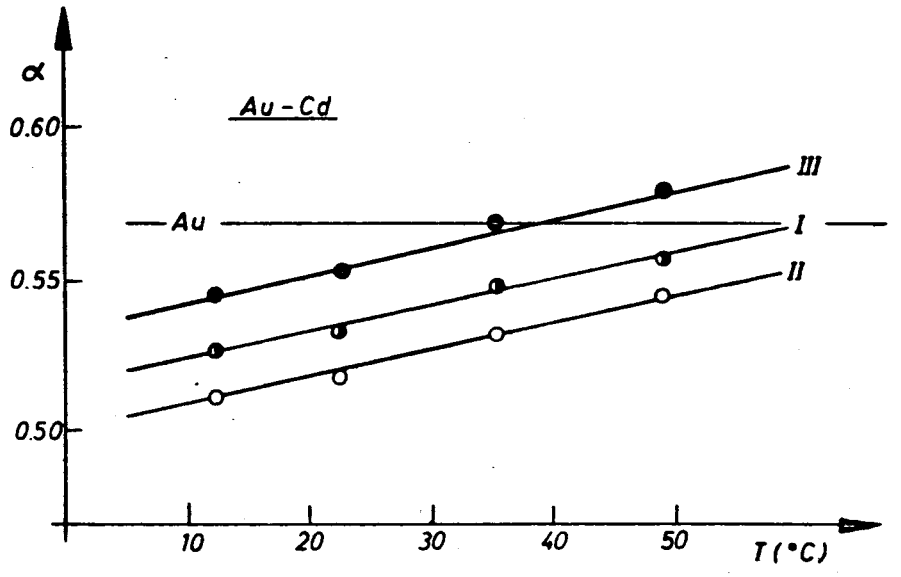
which has the value b = 116 mV for α = 1/2 and T = 20° C. The throughput factors obtained lie somewhat above 0.50.

(6) The throughput factors are independent of temperature for the pure metals (Fig. 25). In the alloys, they generally appear to rise with temperature; Figure 26 shows a few examples of this. The temperature dependence is approximately uniform for the different alloys. Assuming a linear relationship, a rough determination of the temperature coefficients gives us $\frac{\partial \alpha}{\partial T} \approx 0.001$ degrees^{-1}.

4b. Data Given in the Literature

In the case of a few of our cathode metals, studies using the older, less reliable method are available; they are limited to overtension measurements at room temperature. The information regarding the experimental conditions and reproducibilities are incomplete in many respects; in addition, the data from the literature /71





Figs. 25 and 26. Temperature Curves of the Throughput Factors for Copper, Gold and Gold-Cadmium Cathodes.

have only a limited value for comparison owing to the predominantly different electrode preparations and electrolyte conditions. However, we shall present a brief survey.

Our findings for copper (at 20° C) are in very good agreement with the data given in [87] for 0.1n sulfuric acid, which were the most reliable figures previously available. A qualitatively similar overtension behavior was also found for 1n sulfuric acid by Gerischer and Mehl [88].

Hydrogen overtension on gold has been measured many times; the data from the literature were collected and discussed in [70a]. The results for this metal show considerable variation. Especially remarkable in this respect are the differences in the b-values, to which we shall return in the next section.

A few measurements for some of the copper alloys with which we have been concerned can be found in [89]; the uthor describes an increase in overtension for these alloys. On the other hand, Cremer and Kerber [90] found a decrease in overtension relative to pure copper in Cu-Zn (brass). It is not clear from their description, however, which alloy phase was involved.

No data are available for gold alloys. The reader is again referred to [69].

4c. Reaction Mechanisms

The Tafel slopes (b-values) which were found clearly show that in all of our experimental systems, either the Volmer step or the Horiuti step determines the kinetics. According to [88] as well as [37] and [91], the Hoiuti step determines the rate for the formation of hydrogen on copper.

According to the interpolation experiments of Gerischer and Mehl, the Horiuti step also determines the rate for gold. /72

As we have said, the data from the literature show a highly non-uniform pattern for this metal. Aside from considerable differences in the overtension figures, different Tafel slopes were found, corresponding to different reaction mechanisms, so that e.g., b = 27 mV, which would indicate that the Tafel step must be significant in determining

On the other hand, our investigations, based on a large number of tests, have revealed only one overtension pattern which is basically similar to that of copper; the resultant b-values correspond uniquely to the theoretical slope b = 2.3 RT/αF. This is true notonly for the very precise abrasion measurements, but also for the numerous experiments which were carried out using the older method on un-abraded electrodes which had been prepared in different ways. Hence, we can say that our experiments have led to a

reliable determination of the overtension properties which are really characteristic for compact gold[31].

The findings indicate a mechanism similar to that of copper. For reasons of analogy, such an agreement also appears to be more plausible than behavior which is essentially different. Our results are in complete agreement with the kinetic studies of Gerischer and Mehl and with the theories of these authors, according to which the Horiuti step must determine the rate for all metals with smaller overtensions than copper, so long as a discharge step determines the kinetics in them.

Silver occupies a special position among the Ib-metals in a different respect. Thus, it does not seem surprising that there should be differences in its overtension behavior as well, such as we found in our abrasion tests or as were noted in the literature. Gerischer and Mehl found that the Volmer step determined the rate for silver; however, they also discuss a slow Horiuti step and the possibility of a change in the mechanism [55, 92, 68].

5. Conclusions Regarding the Absolute Potential

The activation enthalpy of the rate-determining step of the electrode reaction must always have a nonvanishing value: /73

$$\Delta H^{\pm} > 0.$$

This qualitative condition permits us to make definite statements regarding the values of the absolute equilibrium potentials $\bar{\bar{\varepsilon}}_M$, without knowing $\Delta H^{\pm}$ more precisely, on the basis of overtension investigations which supplement the thermodynamic methods of estimation. By solving the formulas for the exchange flux densities and the experimental activation energies for the equilibrium potentials, we obtain (for a = 1):

$$\bar{\bar{\varepsilon}} = -a_T + b \log J_0 - \frac{\Delta H^{\ddagger}}{\alpha F}$$

$$= \frac{1}{\left(1 - \frac{T}{\alpha}\frac{\partial \alpha}{\partial T}\right)}\left(-a_T + b \log A - b/2{,}3 + T\frac{\partial \bar{\bar{\varepsilon}}}{\partial T} - \frac{\Delta H^{\ddagger}}{\alpha F}\right)$$

as well as

$$\bar{\bar{\varepsilon}} = \frac{1}{\left(1 - \frac{T}{\alpha}\frac{\partial \alpha}{\partial T}\right)}\left(\frac{q}{\alpha F} - b/2{,}3 + T\frac{\partial \bar{\bar{\varepsilon}}}{\partial T} - \frac{\Delta H^{\ddagger}}{\alpha F}\right)$$

---

[31] See [70a] for a discussion and interpretation of the various findings.

All of the values in these expressions up to the $\Delta H^{\pm}$-values can be determined by overtension measurements.

We shall carry out the numerical estimates for copper and gold, since the throughput factors are constant in these metals and therefore the calculation does not involve any temperature coefficients $\frac{\partial \alpha}{\partial T}$, which have been investigated in less detail so far. Using the corresponding experimental values, we obtain the following absolute potentials (at T = 296° K):

$$\bar{\varepsilon}_{Cu} = 1{,}28 - 0{,}08\, \Delta H^{\ddagger}_{Cu} \quad \text{(Volt)}$$
$$\bar{\varepsilon}_{Au} = 1{,}12 - 0{,}08\, \Delta H^{\ddagger}_{Au} \quad \text{(Volt)}$$

The activation energies can be inserted in the above in caloric units (kcal).

From $\Delta H^{\pm} > 0$, we have as the limiting condition: /74

$$\bar{\varepsilon}_{Cu} < +1{,}28 \text{ Volt}$$
$$\bar{\varepsilon}_{Au} < +1{,}12 \text{ Volt}$$

The values of the $\Delta H^{\pm}$ are not known; however, we can assume that they must be on the order of about 10 kcal/mole. This also means that the absolute potentials can have only very small positive or even negative values.

The potential of the platinum-hydrogen normal electrode, which is of particular significance as a basic reference electrode, according to the relationships

$$\bar{\varepsilon}_{Pt} = \bar{\varepsilon}_{Cu} - \frac{1}{e_0}\left(\Phi_{Pt} - \Phi_{Cu}\right) = \bar{\varepsilon}_{Au} - \frac{1}{e_0}\left(\Phi_{Pt} - \Phi_{Au}\right)$$

is somewhat more negative than that of a copper or gold electrode, because $\Phi_{Pt} > \Phi_{Au}, \Phi_{Cu}$ for the work functions of the metals.

CHAPTER IX. CONTACT CHEMICAL EVALUATION

/75

The contact chemical discussion of the overtension findings leads to interesting conclusions regarding the elementary contact-substrate interaction on the hydrogen electrode, and regarding the corresponding critical factors, which are also important for an understanding of the general contact behavior of metals. An examination of the activation energies shows that the interaction energy picture is determined to a considerable degree by the electronic factor, because the latter influences the adsorptive properties of the contacts. The macroscopic overtension behavior is the result of the interplay of the energetic-electronic and special geometric relationships, to the extent that these determine the reaction frequency and the states which are characterized by the reaction entropies in the reaction process. The frequency factors provide us with definite information regarding these geometric problems.

We can present a qualitative interpretation of the entire experimental material which is obviously free of any contradiction. However, even the numerical estimates constitute a picture which not only seems correct in itself but also is in a surprisingly good quantitative agreement with comparable data from adsorption and catalysis and with estimates prepared in completely different ways. For the reasons given earlier, certain assumptions regarding the absolute potentials form the basis of these calculations; the resultant uniformity of the picture appears to us to constitute a further confirmation of their correctness.

Our investigations have revealed differences in the amounts of the throughput factors and in their behavior with temperature. In view of the present status of the data which we have in this regard, it would be premature to make any definite interpretations. Therefore, we will content ourselves on this point with a brief discussion. We will also attempt to show that no fundamental errors will be incurred in the other evaluations by a formal consideration of these differences.

1. INTERACTION ENERGY AND ELECTRONIC FACTOR

In Figures 27 and 28, we have plotted the experimental activation energies for the different types of cathode in the copper and gold groups against the alloy composition. The electron con-

centration EC (Chapter VII) has been selected as a correlation parameter; the values for the different types of alloys show a better coincidence of values for this variable than for a curve plotted against the pure additive content, as we would expect for an energy picture determined by the electronic factor. /76

The diagrams show a regular decrease in the activation energies with increasing electron concentration, which is basically similar for all types of alloys in both groups[32].

1a. Pattern of the Real Activation Enthalpies $\Delta H_H^{\ddagger}$

The uniform behavior of the q-values in all cases is indicative of a high probability that the process of the Horiuti step which determines the rate for our electrodes is made energetically easier with increasing electron concentration in the cathode alloys, i.e., this means that the critical comparison values $\Delta H_H^{\ddagger}$ also exhibit a uniform behavior.

To explain this statement, let us use first the relationship derived in Chapter V:

$$\Delta H_L^{\ddagger} - \Delta H_M^{\ddagger} = q_L - q_M + \left[\left(\frac{\partial \alpha_L}{\partial T} - \frac{\partial \alpha_M}{\partial T}\right) T - \Delta \alpha_{LM}\right] F \bar{\bar{\varepsilon}}_M + \left[\left(\frac{\partial \alpha_L}{\partial T}\right) T - \alpha_L\right] F \kappa_{LM}$$

for the relative values of $\Delta H^{\ddagger}$ and q [33]. A numerical estimate of the terms with $\bar{\bar{\varepsilon}}_M$ and κ_{LM} on the right-hand side will show whether the $\Delta H^{\ddagger}$ and q behave similarly. For the factors of $\bar{\bar{\varepsilon}}_M$ and κ_{LM}, our findings yield the following as extreme values ($T = 300^{\circ}$ K): + 8.0 kcal/volt mole -5.7 kcal/volt mole. In the least satisfactory case, we therefore obtain:

$$\Delta (\Delta H^{\ddagger})_{LM} = \Delta q_{LM} + 8{,}0\ \bar{\bar{\varepsilon}}_M - 5{,}7\ \kappa_{LM} \quad \text{(kcal/Mol).}$$

($\bar{\bar{\varepsilon}}$, κ in Volt)

[32] It may be that this involves relatively small changes in values whose determination involves errors from a number of evaluations (current-potential curves → Tafel parameters → exchange flux densities → Arrhenius parameters).

[33] L = alloy; M = basic metal (or alloy with a smaller amount of admixture than L. As long as there is no indication of the reaction-determining step, we will be concerned in the following with the values for the Horiuti step.

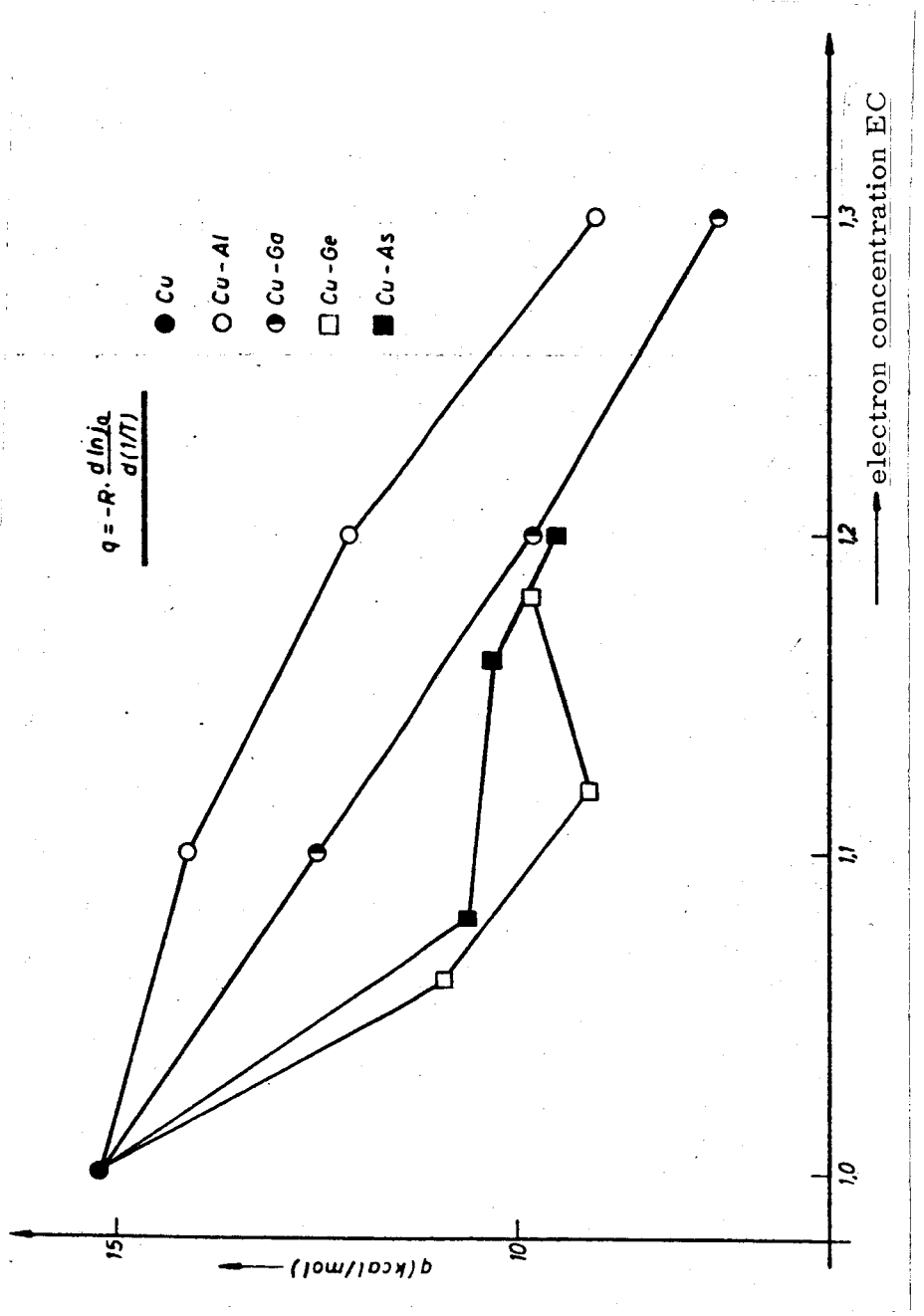


Fig. 27. Experimental Activation Energies of Cathodic Hydrogen Dissociation on Copper Alloys.

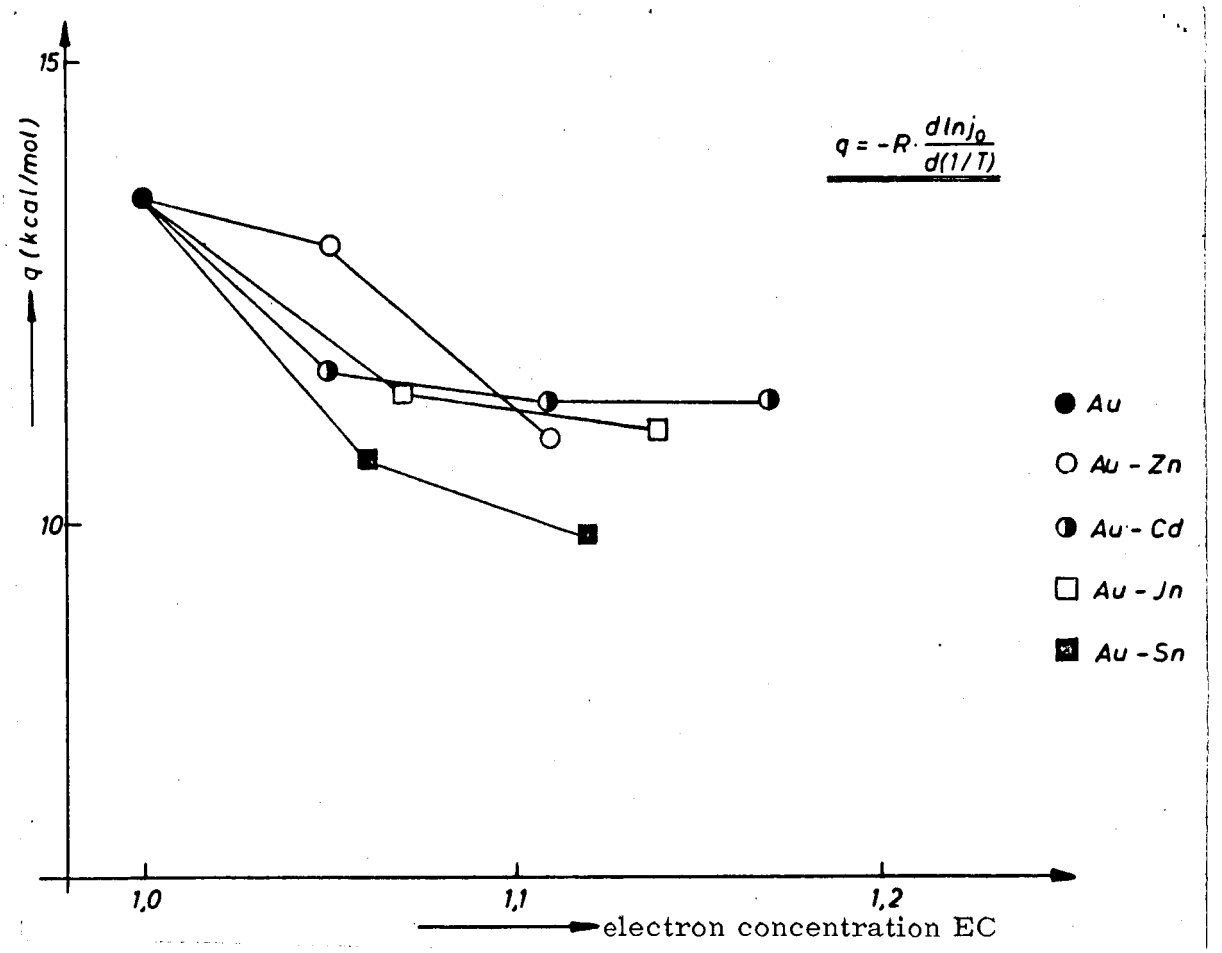


Fig. 28. Experimental Activation Energies of Cathodic Hydrogen Dissociation on Gold Alloys.

No measurements of contact potentials or work functions have /77
been available thus far for the alloys with which we are concerned. On the basis of available values of work potentials for various metals, we can assume that the contactpotentials do not exceed a value of 0.1 V; they are probably positive ($\Phi_L < \Phi_M$). In the present study, therefore, the κ-term can be disregarded.

With respect to the absolute potentials $\bar{\bar{\varepsilon}}_M$ of our basic metals copper and gold, we have found (Chapter VIII.5) that they usually have very small positive values and probably can even have negative values as well. The correctness of this assumption is supported both by the condition $\Delta H^{\pm} > 0$ for the rate-determining step, but also by the fact that for absolute potentials which are positive and greater (but still remain below the extreme values of + 1.28 and + 1.12 V) show a qualitatively nonuniform pattern for the activation enthalpies $\Delta H^{\pm}$, and this would be very difficult to understand.

The estimates which have been made here on the basis of the extreme case show that the $\Delta H^{\pm}$ and q vary symbatically. The experimental activation energies therefore provide a qualitatively correct idea of the behavior of the true activation enthalpies; the relative variations also correspond quantitatively to a considerable degree; the individual values are either approximately the same or a few kcal/mole larger for the $\Delta H^{\pm}$, if we assume that the absolute potentials are between - 0.5 and + 0.1 V. Various arguments point to this range (see above and Section 1c of this chapter).

1b. Activation Enthalpies and Adsorption Energies of Hydrogen on Metals

From the energy diagrams ("Lennard-Jones" diagrams) of the electrode reaction, we can see that differences in the activation enthalpies $\Delta H^{\pm}$ (at the same polarization $\varepsilon = 0$) are caused exclusively by differences in the adsorption energies of the participants in the reaction of the rate determining elementary step, which are bound adsorptively to the electrode metal. The Horiuti step determines the kinetics for both copper and gold. The discussion of Lennard-Jones curves for this elementary step reveals an inverse dependence of the activation enthalpy $\Delta H^{\pm}_{H,M}$ on the heats of adsorption ΔH_H Ⓜ of the atomically adsorbed hydrogen involved in the reaction (H Ⓜ); in this case, the adsorbed hydrogen belongs to the original system (H^+_{aq} + e^-(M) + H Ⓜ), whose energy (approximately $G_{(H^+_{aq} + e^-(M) + H\,Ⓜ)}$) and energy curve are displaced toward higher values, e.g., as the adsorption energy becomes more positive (i.e., smaller). However, such a displacement results in a lowering of the activation peak. The relationships are discussed below in another connection (Fig. 29).

The conditions are reversed for a rate-determining Volmer step. /78
In the Volmer reaction, the adsorbed hydrogen is the reaction prod-

uct ($H^+_{aq} + e^-(M) + Ⓜ \rightarrow H Ⓜ$); with decreasing adsorption energy $\Delta H_{H Ⓜ}$, the product-energy curve is raised, which has the same significance as a drop in the reactant curve, i.e., a raising of the activation peak[34].

As far as the adsorption properties of atomic hydrogen are concerned, our findings initially led to the result that the adsorption energy decreases with increasing impurity contact in Hume-Rothery alloys, so that the interaction becomes weaker. We can also conclude that the critical contact parameter in this case is the degree of electron saturation of the contact, which we have designated somewhat formally by the electron concentration EC. In the terminology of the electronic factor in catalysis, the present investigations of hydrogen adsorption on metals would constitute a "donor process" and the atomic hydrogen would be a "donor particle" in heterogeneous interactions.

These data are of importance for a valid explanation of critical questions of adsorption and catalysis, which have been the subject of highly diverse opinions in the past. In this connection, we should like to mention once again (cf. Chapter V), that the concept of "donor" does not necessarily involve loss of an electron, but (in a more general sense) expresses the tendency of a particle to interact with "electrophilic" partners.

In this regard our data support the findings which were developed in particular by Schwab in numerous catalytic investigations. We will only mention here the measurements of the dissociation of formic acid, carried out, like those in this work, with Hume-Rothery alloys [27-31]. These experiments showed a rise in activation energy with addition of impurities; Schwab's interpretation is based on the assumption of a decreasing tendency toward hydrogen adsorption with increasing filling of the Brillouin zones of the contact. At first glance, our findings appear to contradict this; however, the decrease in activation energy which we found shows that there is a decrease in the adsorption energy of the atomic hydrogen, as we have seen.

The amounts of the changes in activation energy for the electrode reaction correspond roughly to those found by Schwab for dissociation of formic acid in the same α-phases.

1c. Numerical Aspects /79

We shall now discuss the quantitative relationships. For lack of a knowledge of the actual absolute potentials, we will calculate the amounts of the energy values ($\Delta H^{\ddagger}$ and $\Delta G^{\ddagger}$) for the $\bar{\bar{\varepsilon}}_M$-

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[34] Clearly, a knowledge of the reaction mechanism is a prerequisite for comparing the activities of various electrodes; this is a fact which has not always been taken into account in the past.

values assumed and investigate the consistency of the findings on the basis of the results obtained. We shall select the values given above of $\bar{\bar{\varepsilon}}_M$ = + 0.1 V and $\bar{\bar{\varepsilon}}_M$ = - 0.5 V as the approximate interval limits within which the true absolute potentials are assumed to lie.

Attempts to calculate the absolute potentials from the reaction sequences of cyclical processes offer no advantages: owing to the inaccurate or absent data on several very necessary and important parameters (surface potentials, hydration energies, work functions), these thermochemical estimates have been much too inaccurate thus far for use here; they do not give any useful information even with respect to the sign of the absolute potential.

For T = 300° K, our calculations show the following:

absolute value $\bar{\bar{\varepsilon}}_M$ (Volt)			- 0,5	+ 0,1
copper	$\Delta H^{\ddagger}_{Cu}$	(kcal/Mol)	22,9	15,2
	$\Delta G^{\ddagger}_{Cu}$		29,9	22,2
gold	$\Delta H^{\ddagger}_{Au}$		21,3	13,5
	$\Delta G^{\ddagger}_{Au}$		28,3	20,5

Using the formula

$$\Delta H^{\ddagger}_M = q_M - RT + \alpha_M FT \frac{\partial \bar{\bar{\varepsilon}}_M}{\partial T} - \alpha_M F \bar{\bar{\varepsilon}}_M$$

the $\Delta H^{\ddagger}$ are obtained. To determine the $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S$, we used an average value of $T\Delta S^{\ddagger}$ = - 7.0 kcal/mole taken from the entropy estimates in Chapter IX.2.

There is also the problem of the adsorption energies ΔH_H Ⓜ of the atomic hydrogen. Only a small amount of data is available, and is listed in Table XI.

TABLE XI. ADSORPTION ENERGIES OF HYDROGEN ON THE Ib-METALS (in kcal/mole) /80

energy value	literature	copper	silver	gold
$\Delta H_{diss.}$	WARD [93]	- 9		
(H_2 + 2 Ⓜ ⟶ 2 H Ⓜ)	ELEY u. ROSSINGTON [94]	- 8,0		
	SHIELD u. RUSSEL [95]	-10		
	ELEY [13]	-13,7		
	COUPER, ELEY et al. [96]	-13,6	-11,5	-13,7

TABLE XI (Continued)

energy value	literature	copper	silver	gold
ΔH_H Ⓜ	calc. with the values from [96]	-58,9	-55,8	-59,0
(H + Ⓜ → HⓂ)	STEVENSON [97]	-64,4		
	HIGUCHI et al. [98]	-63,5		

The values given by Ward and by Shield and Russel come from calorimetric measurements on copper powders, while that of Eley and Rossington was obtained from isotherms for para-hydrogen conversion on copper films. The other values were calculated as initial heats of adsorption (degree of coverage $\vartheta \ll 1$), using the Eley formula.

From these data, we see that the adsorption energies ΔH_H Ⓜ for copper and gold are nearly the same and are $\sim$ -60 to-65 kcal/mole; for silver, on the other hand, somewhat smaller values must be assumed.

Sometime ago, Gerischer [73], in a general theoretical analysis, discussed the relationship between the mechanism of electrolytic hydrogen dissociation and the adsorption energy of atomic hydrogen, and carried out numerical estimates as well; in these calculations, based on the method of cyclic processes, special selection of the reference states avoided the need to discuss the absolute potentials. An important qualitative result of this is that a switch in the reaction-determining step can be expected in a middle range of heats of adsorption on the basis of the opposing dependencies of the activating energies of the Volmer and Horiuti steps, previously discussed in Chapter IX.1. The relationships are shown in Figure 29 in comparison to those of Gerischer. From the latter, we shall use the following assumptions for our considerations: /81

(1) The Volmer and Horiuti steps determine the reaction for smaller and larger adsorption energies, respectively. The changeover occurs approximately at ΔH_H Ⓜ = -55 kcal/mole.

(2) The free activation enthalpies $\Delta G_V^{\ddagger}$ and $\Delta G_H^{\ddagger}$ in the transition region amount to 15-20 kcal/mole; for the Volmer step, they increase antibatically (for the Horiuti step, symbatically) with the value of the heat of adsorption (Fig. 30).

Gerischer's calculations contain considerable simplifications and assumptions in determining the values of some of the energy parameters entering into the balance; we ourselves were unable to determine the energies with the true absolute potentials, but only for limited values of the latter, which were chosen somewhat ar-

bitrarily but completely independently of Gerischer's results. Finally, the hydrogen adsorption energies have still not yet been determined very precisely. Naturally, this means that variations in the details of the numerical data are still possible. However, comparison shows a practically quantitative and essentially valid agreement of the findings. This is a strong argument for the correctness of the various estimates and also indicates the freedom from contradiction in the presentation of our entire body of material.

For copper and gold, in which the Horiuti step determines the kinetics, the free activation enthalpies $\Delta G^{\pm}$ are on the order of 20 to 30 kcal/mole. This means that they are in complete agreement with the hydrogen adsorption energies expected for these metals and clearly lie in the "Horiuti range" of Gerischer. The activation enthalpies $\Delta H^{\pm}$, which are about 8 kcal/mole smaller, decrease in the α-phases by about 5-8 kcal/mole because the adsorption energy of the atomic hydrogen decreases with increased impurities. This decrease still lies within the Horiuti range, as shown in Figure 30. In the alloys with the smallest activation energies, the transition region is probably reached, in which case a real explanation could be found under the conditions of certain irregularities in the q-diagrams (Figs. 27 and 28)[35]. /82

In the case of silver, hydrogen adsorption is known to be markedly less[36], so that perhaps the transition to the Volmer mechanism occurs in this metal or in the range of its α-alloys. We have already mentioned that silver actually occupies a special place with regard to overtension behavior and with regard to other contact-chemical characteristics as well.

The electrode potentials of copper and gold differ in their contact potential. From the relationships developed in Chapter VIII.5, we obtain:

$$\bar{\varepsilon}_{Cu} - \bar{\varepsilon}_{Au} = \kappa_{Cu\,Au} = 0{,}16 - 0{,}08\,(\Delta H^{\ddagger}_{Cu} - \Delta H^{\ddagger}_{Au})\ \text{(Volt)}.$$

The contact potential $\kappa_{Cu\,Au}$ $(= -(\Phi_{Cu} - \Phi_{Au})/e_0$ can be calculated from the work functions. The data given in the literature differ in this regard; the following are given as the "most reliable values" [38, 100] for the polycrystalline metals: $\Phi_{Cu} = 4.46$ eV and $\Phi_{Au} = 4.46$ eV [101] (contact-potential method), as well as $\Phi_{Au} = 4.72$ to 4.82 eV [102] (photoelectric method). The value

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[35] The transition problem will be solved later by studies of the mechanism on the cathodes in question.

[36] This is also indicated by spectroscopic findings. According to [99], the M-H-bonds of Ib-metals have the following binding energies: CuH: 66.5 kcal/mole; AgH: 57.7 kcal/mole; AuH: 71.3 kcal/mole.

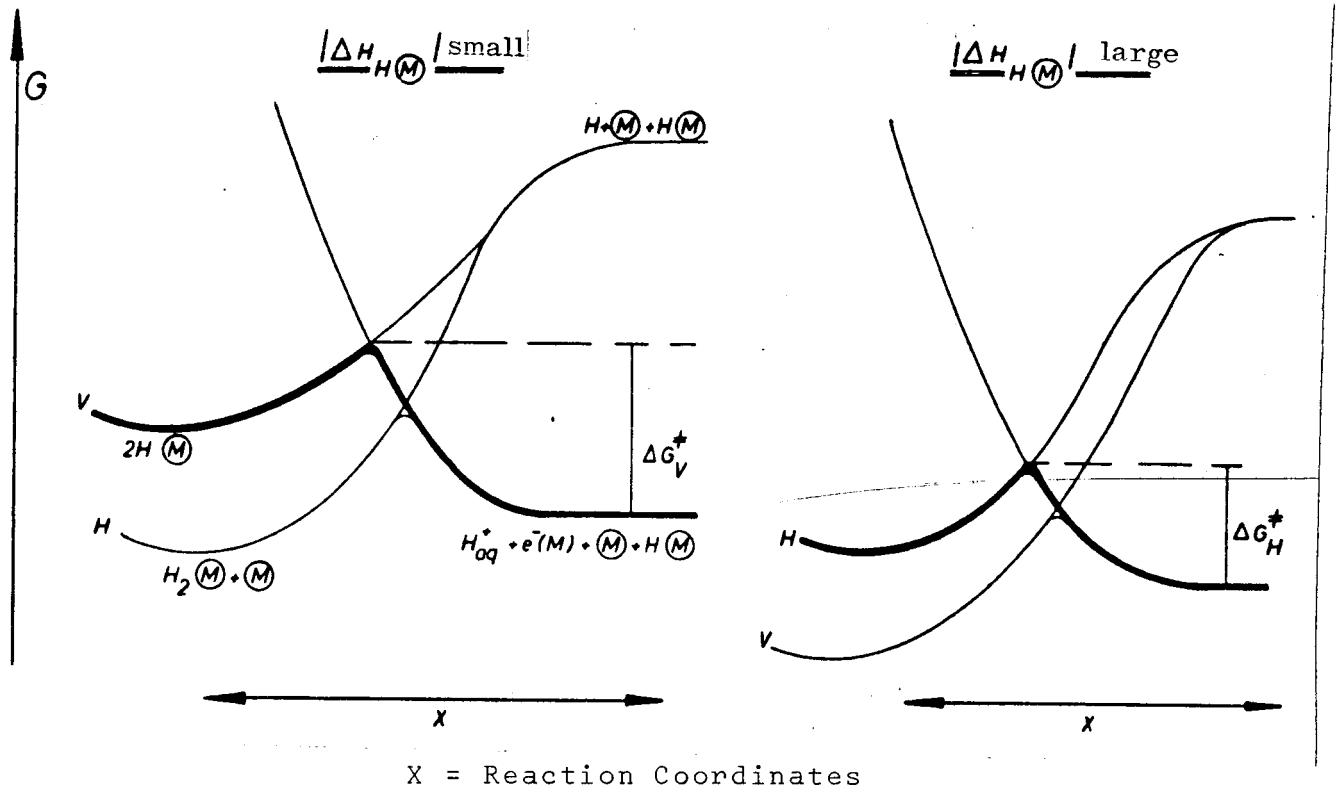

Fig. 29. Reaction Energies of the Volmer and Horiuti Steps with Weak and Strong Hydrogen Adsorption. Lennard-Jones Diagrams Drawn Schematically after Gerischer.

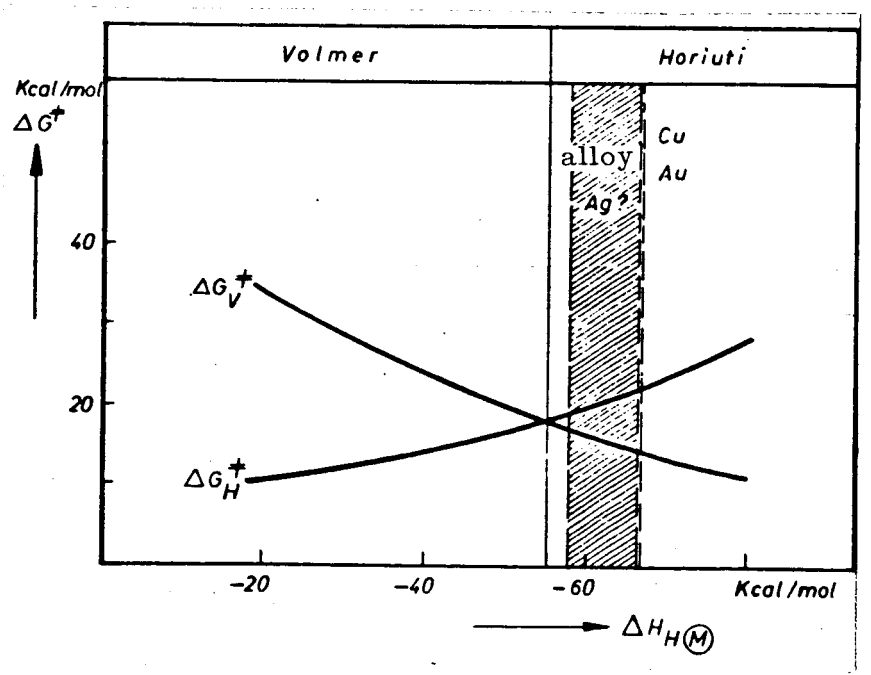

Fig. 30. Free Activation Enthalpies of the Volmer and Horiuti Steps vs. Adsorption Enthalpy of Atomic Hydrogen (After Gerischer). Probable Range for the Cathode Systems Investigated.

of $\kappa_{Cu\ Au}$ can then vary from 0 to +0.36 V, i.e., the librium potential of the gold electrode is perhaps somewhat more negative than that of the copper electrode. In general, we find that the activation enthalpies $\Delta H^{\ddagger}_{Cu}$ and $\Delta H^{\ddagger}_{Au}$ cannot be markedly different (maximum difference ~ 2 kcal/mole). This finding also fits well into the total picture, because copper and gold (in accordance with their homologous character) should have very similar interaction activities with respect to the discharge and adsorption of hydrogen.

2. DISCUSSION OF FREQUENCY FACTORS

/83

In our experimental systems, we have a Volmer-Horiuti mechanism, with the Horiuti step determining the reaction probably in all cases. We know, thereore, that stereochemical contact factors in the narrower sense, which could influence the reaction energy picture, will not be influential here. In both elementary reactions, in contrast to the Tafel step, the interactions take place exclusively between single centers or adsorption partners (Ⓜ or H Ⓜ) and free reactanta ($H^{+}; e^{-}$ (M)).

Further information is contained in the frequency factors, which (according to the theory given in Chapter V.2) are determined as follows:

$$J_{o\,M} = \frac{2FkT}{h} N_M \exp \frac{\Delta S^{\ddagger}_{(M)}}{R}$$

They acquire their individual values depending on the various N_M and $\Delta S^{\ddagger}$ of the reaction systems. The number of centers N_M is a specific geometric contact parameter; the activation entropies are the result of the special motion and order states of the reactant groupings in the critical elementary step; hence, their values probably constitute mainly the pure characteristic values for the various mechanisms, which otherwise depend specifically on the type of cathode only in certain special cases.

2a. Numbers of Centers and Activation Entropies

On the basis of their similar overtension behavior, we assumed for our basic metals copper and gold that the activation entropies $\Delta S^{\ddagger}_{Cu}$ and $\Delta S^{\ddagger}_{Au}$ would have the same value. The same could be expected for the numbers of centers N_{Cu} and N_{Au} as far as the order of magnitude is concerned. Hence, roughly the same frequency factors should be obtained in the cathode metals.

The experimental findings are actually in very good agreement with this proposition; we find the following values:

	log A	log J_0
copper	4,06	3,63
gold	4,00	3,57

The differences lie well within the limits of error; it should be pointed out however that the ratio between these values (J_{0Cu}/J_{0Au} = 1.15) lies in the same direction and order of magnitude as (with assumption of equal distribution of the crystal surfaces) the atomic-number ratio of the unit surface, which is calculated with the lattice constants a_{Cu} = 3.61 Å and a_{Au} = 4.07 Å to give a value of (a_{Au}/a_{Cu}) = 1.28.

The Tafel slope b ◻ 2.3 RT/αF (theoretical value: 116 mV), /84
found by us for the case where the Horiuti step determines the rate, indicates that the mechanism designated by the number IIa (cf. III.3) is present, in which the electrode is completely covered with chemisorbed hydrogen ($\vartheta \approx 1$).

For gold cathodes (in 2n- or 8n H_2SO_4), the degree of coverage at equilibrium potential is ϑ = 0.03 to 0.04 [103, 104]. No accurate data are available for copper; Hickling and Taylor [105] were unable to determine any measurable coverage. The findings were obtained under the same experimental conditions as ours; our data are based on highly cathodic polarization regions, and it is likely that other reaction conditions are present at equilibrium potential. Probably, however, these data are also valid for our measurement ranges as far as the order of magnitude is concerned.

A slight surface coverage does not contradict the idea of chemisorptive saturation, as it requires the special kinetics IIa. A distinction must be made between the "gross" degree of coverage of a contact surface (determined by the abovementioned authors) and a "net" degree of coverage which is critical for the kinetic formulations. Gross and net degrees of coverage are not necessarily identical. As we know, only partial regions of a contact surface often participate in the interaction portion of a given reaction. The data on the centers which are occupied or occupiable in a particular process are based on these partial regions alone, whose area density amounts to a total of N_{active} for the kinetically critical net degree of coverage, we have: $\vartheta \triangleq$ occupied fraction of N_{active} and, if N_{total} represents the area density of all (active + inactive) surface sites, we will have:

$$\vartheta_{net} = \vartheta_{gross} \times \frac{N_{total}}{N_{active}}$$

It may be that even in our systems there is the case N_M (= N_{active}) < N_{total}, because it may be that only certain crystal faces or regions of the polycrystalline inhomogeneous cathode surfaces are capable of hydrogen adsorption, and that their nature and distribution are practically the same for copper and gold.

There are about 10^{15} atoms/cm² of surface. If we adopt the /85
above viewpoint, we then obtain:

$$N_M = 10^{14} - 10^{15} \frac{\text{atom}}{\text{cm}^2} = \frac{10^{-9}}{6.0} - \frac{10^{-8}}{6.0} \frac{\text{g-atom}}{\text{cm}^2}$$

We then obtain as the activation entropy $\Delta S_H^{\pm}$ of the Horiuti step:

$$\Delta S_H^{\bullet} \approx -22 \text{ bis } -26 \text{ cal/ mole degree}$$

A value of this size appears reasonable; its sign indicates that the degrees of freedom of motion are lost in the transition $H_{aq}^{+} + H\,Ⓜ + e^{-}(M) \rightarrow [H;H\,Ⓜ]^{\pm}$ of the initial system into the activated intermediate state.

2b. Decrease of the Frequency Factor in Alloys

The frequency factors for the alloyed cathodes decrease up to a few orders of magnitude relative to those for the basic metals. At the present time, we are unable to give a definite interpretation for this decrease. Undoubtedly it does not involve a purely numerical reduction in the number of centers. Several viewpoints indicate a possible explanation on the following basis: in the case of the alloys with which we are concerned, atoms of the added metal are present on the surface and possess an electronegativity different from that of the atoms of the basic metal and a rather base character. This results on the one hand in an inhomogeneity of the electrical surface field, and on the other hand a tendency toward detachment of the ions. We can assume that in the case of these alloys, many positively charged ions of the added metal are adsorbed within the double layer on the electrode surface; this happens to a limited extent, of course. It is possible that these Ad-ions, due to a pronounced and extensive Coulomb effect, shield large areas of the surface against contact with the reacting protons and thereby produce an apparent reduction in the number of centers. In addition, we have also to reckon here with occasional changes in the activation entropies, which likewise produce a variation of the values of the frequency factors. Perhaps the θ-relationships which were found also share this basis (i.e., a $\Delta S^{\pm}$ - $\Delta H^{\pm}$ relationship.

The potential relationships of the double layer, modified by Ad-ions and surface inhomogeneities, are taken into account in the reaction energy picture by the values of the throughput factors. /86
The particular behavior of these values with temperature in alloys is also closely related to special surface properties of these cathodes; in any case, this cannot be a matter of a general effect such as a temperature dependence of the double layer structure in contact with the electrolyte, because a similar effect would have to be observed in pure copper and gold as well.

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